raphs on Industrial Chemistry

CATALYSIS IN DUSTRIAL CHEMISTRY

G. G. HENDERSON

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MONOGRAPHS ON INDUSTRIAL CHEMISTRY

Edited by Sir EDWARD THORPE, C.B., LL.D., F.R.S.

Emeritus Professor of General Chemistry in the Imperial College of Science and Technology, South Kensington; and formerly Principal of the Government Laboratory, London.

INTRODUCTION

DURING the last four or five decades the Applications of Chemistry have experienced an extraordinary development, and there is scarcely an industry that has not benefited, directly or indirectly, from this expansion. Indeed, the Science trenches in greater or less degree upon all departments of human activity. Practically every division of Natural Science has now been linked up with it in the common service of mankind. So ceaseless and rapid is this expansion that the recondite knowledge of one generation becomes a part of the technology of the next. Thus the conceptions of chemical dynamics of one decade become translated into the current practice of its successor; the doctrines concerning chemical structure and constitution of one period form the basis of large-scale synthetical processes of another; an obscure phenomenon like Catalysis is found to be capable of widespread application in manufacturing operations of the most diverse character.

This series of Monographs will afford illustrations of these and similar facts, and incidentally indicate their bearing on the trend of industrial chemistry in the near future. They will serve to show how fundamental and essential is the relation of principle to practice. They will afford examples of the application of recent knowledge to modern manufacturing procedure. As regards their scope, it should be stated the books are not intended to cover the whole ground of the technology of the matters to which they relate. They are not concerned with the technical *minutiæ* of manufacture except in so far as these may be necessary to elucidate some point of principle. In

some cases, where the subjects touch the actual frontiers of progress, knowledge is so very recent and its application so very tentative that both are almost certain to experience profound modification sooner or later. This, of course, is inevitable. But even so such books have more than an ephemeral interest. They are valuable as indicating new and only partially occupied territory; and as illustrating the vast potentiality of fruitful conceptions and the worth of general principles which have shown themselves capable of useful service.

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George Gerald

BY

G. G. HENDERSON

M.A., D.Sc., LL.D., F.R.S.

"Freeland" Professor of Chemistry, The Royal Technical College, Glasgow

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PREFACE

In compiling this short monograph I have availed myself freely of the information contained in a number of books in which the subject of Catalysis is discussed, and am specially indebted to the following—

Sabatier, *La Catalyse en Chimie Organique.*
Jobling, *Catalysis.*
Carleton Ellis, *The Hydrogenation of Oils.*
Weyl, *Die Methoden der Organischen Chemie.*
Allmand, *Applied Electro-Chemistry.*

The *Journal of the Society of Chemical Industry* has been an invaluable source of abstracts of patent specifications, of abstracts of papers published in other journals, and of original communications.

The monograph will serve, I hope, to indicate the number and variety of the industrial applications of catalysis, and to suggest the desirability of further work in this most promising field of investigation.

G. G. H.

The Royal Technical College,
Glasgow,
July, 1918.

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ABBREVIATED TITLES OF JOURNALS TO WHICH REFERENCES ARE MADE

Abbreviated Title.	Journal.
Ann.	Liebig's Annalen der Chemie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Bull. Soc. chim.	Bulletin de la Société Chimique.
Chem. Soc. Trans.	Transactions of the Chemical Society.
Chem. Trade Jour.	The Chemical Trade Journal.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
J. Am. Chem. Soc.	Journal of the American Chemical Society.
J. Gas Lighting	The Journal of Gas Lighting.
J. Ind. and Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.

Abbreviated Title.	Patent Literature.
Eng. P.	British Patent.
Fr. P.	French Patent.
D. R. P.	German Patent.
U.S. P.	United States Patent.

CATALYSIS IN INDUSTRIAL CHEMISTRY

CHAPTER I

Catalysis and Catalysts

The term "catalysis" is now generally used to designate those chemical changes of which the progress is modified by the presence of a foreign substance, and the agent which induces the effect is called the "catalyst." It has for long been known that the velocity of many chemical reactions which take place very slowly if the reacting substances alone are present in the system is greatly increased by the addition of certain substances which have the same composition after the change has been completed as at the beginning, and which therefore appear to influence the course of the reaction without taking any definite stoichiometric part. It is now recognized that the phenomenon is of very general occurrence, and the importance of the study of the subject is sufficiently demonstrated by statement of the fact that the employment of catalysts enables the technical chemist to carry out a large number of manufacturing processes which otherwise would be economically impossible.

At one time the idea prevailed that catalytic actions are the exception rather than the rule, but our constantly increasing knowledge of the enormous number and variety of the chemical changes which are susceptible to catalytic influences has shown that this opinion is very far from being correct. There are, indeed, good grounds for accepting Ostwald's statement that there is probably no reaction which cannot be influenced catalytically, and no substance,

whether elementary or compound, which cannot act as a catalyst.

Catalytic actions are of two kinds, homogeneous and heterogeneous. The former class includes reactions between gases which are promoted by a gaseous catalyst, and those in which the catalysis is due to some substance which is in solution in the liquid in which the reaction is taking place. A typical example of the latter is the conversion of cane sugar into dextrose and lævulose in aqueous solution. At the ordinary temperature the reaction $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$ takes place very slowly; when, however, a strong acid such as hydrochloric acid is added to the solution the speed of the change is greatly increased; in dilute solutions the velocity is proportional to the concentration of the hydrogen ions.

As regards gaseous systems, the influence of catalysts is illustrated by the effect of water vapour in inducing the combination of carbon monoxide and oxygen. As was shown by Dixon, the dry gases will not unite; the presence of water vapour, or of substances which will form water vapour under the conditions of the experiment, is essential, since the reaction takes place in two stages, as represented in the following equations :—

(1) $2CO + 2H_2O = 2CO_2 + 4H$,
(2) $4H + O_2 = 2H_2O$.

The cases of heterogeneous catalysis fall into two groups—

(1) Catalysis of a gaseous reaction by the introduction of a solid; for example, in the well-known contact method for the production of sulphuric anhydride the combination of sulphur dioxide and oxygen is induced by the catalytic action of spongy platinum.

(2) Catalysis of a reaction occurring in a solution by addition of a solid or of particles such as are found in colloidal solutions of metals or of enzymes; as, for instance, in the hardening of oils or liquid fats by treatment with hydrogen in presence of finely divided nickel.

In heterogeneous catalysis the activity of the catalytic

agent is largely dependent upon its physical state; as a general rule the finer the state of division the greater the activity. Thus platinum black is far more efficient than spongy platinum, and this in turn than the compact metal, whilst maximum activity is attained when the metal is reduced to the extreme state of subdivision in which it exists in colloidal solutions.

There is room for much difference of opinion as to the part actually played by a catalyst in a reaction which is influenced by its presence, and, indeed, it is only necessary to consider the great diversity of catalytic reactions in order to realize the difficulty of formulating an explanation of the mechanism of catalysis which will be applicable to all cases. The theories which have been advanced to explain the mechanism of catalysis fall into two classes, the chemical and the physical. The former asserts that the effect of the catalyst is to be attributed to the continuous formation and decomposition of unstable intermediate products; whilst the physical theory explains the phenomena as being due to the condensation, or increase in concentration, of the reacting substances at the surface of the catalyst, such increase in concentration being brought about by capillary forces. For a discussion of the rival theories readers are referred to Mellor's *Chemical Statics and Dynamics*, and to Lewis's *A System of Physical Chemistry*, Vol. I. Here it must suffice to state that beyond doubt many catalytic reactions, and probably all which take place in homogeneous systems, depend upon the formation of unstable intermediate compounds, and that it is difficult to understand how the physical theory can afford an explanation of the specific action of catalysts and of the diversity of the effects which they produce. In many cases of heterogeneous catalysis the possibility of the formation of intermediate products is by no means excluded. The effect of metals as catalysts of hydrogenation may be explained on the assumption that metallic hydrides are formed, which under the conditions of the experiment give up their hydrogen to the substance undergoing hydrogenation. The catalytic

action of metals in promoting the combination of nitrogen and hydrogen to form ammonia may be attributed to the formation of metallic nitrides which interact with the hydrogen; and, in fact, nitrides such as uranium nitride are excellent catalysts of the reaction. The dehydrating action of alumina on alcohols may be the result of the formation and subsequent decomposition of aluminium alkyloxides, which, in fact, are known to exist and to break down under the influence of heat; for example, the formation of ethylene from ethyl alcohol may be represented by the following equations:

(1) $Al_2O_3 + 2C_2H_5OH = H_2O + Al_2O_2(OC_2H_5)_2$;
(2) $Al_2O_2(OC_2H_5)_2 = Al_2O_3 + H_2O + 2C_2H_4$.

Many other examples might be quoted, but at the same time it must be admitted that in at least some cases of heterogeneous catalysis the physical theory appears to offer the only explanation of the action of the catalyst.

It was long ago recognized that a catalyst has the same chemical composition at the end of the reaction in which it has exerted an influence as at the beginning, but it must not be concluded that its physical state is necessarily the same after the reaction is over. On the contrary, the change in physical condition which in many cases the catalyst has undergone shows that it has taken an active part in the reaction in the sense that an intermediate compound has been formed. For instance, when ammonia is decomposed into its elements by contact with heated metals there is a complete alteration in the physical state of the latter, which is undoubtedly due to the continuous formation and decomposition of metallic nitrides.

A small, sometimes an infinitesimal, quantity of a catalyst suffices to effect the transformation of an indefinitely large amount of the reacting substances, unless for any reason the activity of the catalyst is reduced, either by the presence of traces of substances which have a deleterious effect or by a change in its physical condition, or unless the catalyst disappears owing to independent side reactions, as

happens to aluminium chloride in Friedel and Crafts' reaction.

Ostwald's definition of a catalytic agent as a substance which changes the velocity of a reaction without itself being changed by the process implies that a reaction must not only be possible but actually in at least slow progress before the catalyst can produce any effect, or, in other words, that a catalyst is not capable of starting a reaction, but can only modify the rate of change. Other chemists, on the contrary, hold that a reaction which is not taking place at all can be started by the addition of a catalyst to the system. Perhaps the difference between the two views is more apparent than real, for, after all, it is not easy to discriminate between a reaction which is not taking place and one which is in progress but of which the progress is too slow to be detected by any means at our disposal.

Since catalysts take no permanent part in many of the reactions which are influenced by their presence, they cannot affect the equilibrium point finally reached, although the velocity of the change may be greatly modified. In balanced actions the final state of equilibrium depends only upon the ratio of the velocities of the direct and the reverse reactions, and since the final state of equilibrium is not affected by the presence of a catalyst, it follows that the velocities of both the direct and the reverse reactions are thereby changed by the same fractional amount. In general the state of equilibrium in a system is independent of both the nature and the quantity of a catalyst present in the system, although in cases where the catalyst disappears to some extent owing to the occurrence of secondary reactions it is clearly possible that the equilibrium point may be shifted.

In some reactions substances are produced which themselves have a catalytic effect on the speed of the change; this phenomenon is called *Autocatalysis.* For example, the hydrolysis of esters by water is greatly accelerated by the addition of acids, and it has been observed that the acid produced by hydrolysis of the ester itself acts

catalytically; hence it is easy to understand why it is that the action of water on an ester proceeds slowly at first and rapidly increases in velocity as the acid accumulates in the system. Again, Veley has shown that the action of pure nitric acid on many pure metals such as silver and copper is very slow, but once begun increases in velocity and may become very violent, because nitrous acid, which acts catalytically, is produced in the reaction.

Most frequently the effect of the presence of a catalyst is to increase the velocity of a chemical change, but many instances of *Negative Catalysis* are known, in which certain substances have an inhibiting effect on the progress of the change. The oxidation of sodium sulphite in aqueous solution by oxygen is much retarded by the presence of very small quantities of such substances as mannitol or benzaldehyde; the addition of a small amount of alcohol inhibits the decomposition which chloroform undergoes in presence of air and light; water, which so frequently has a catalytic effect in promoting a reaction, may also act as a negative catalyst, for example, in retarding the decomposition of oxalic acid by hot concentrated sulphuric acid. Negative catalysis also occurs when one of the reacting substances which has a catalytic influence is gradually withdrawn from the system during the course of the reaction.

The inhibiting action of negative catalysts must be distinguished from the effect of " poisons," or " anticatalysts " on the activity of catalysts. It is frequently observed that catalytic agents lose their efficiency after being in use for some time, and as a rule this is due to the presence of substances which have an injurious influence. In the contact process for the manufacture of sulphuric acid even traces of arsenic compounds in the gases soon render the platinum catalyst quite inactive; in the synthesis of ammonia from its elements iron containing as little as 0·01 per cent. of sulphur is of very little use as a catalyst; when using finely divided nickel as a catalytic agent Sabatier found that traces of bromine in the air of the laboratory rendered it impossible to hydrogenate phenol which had stood there

overnight in an open flask, and that benzene which had not been scrupulously freed from thiophen could not be converted into cyclohexane; in hydrogenations of liquids in presence of palladium, it has been found that when the palladium is deposited on aluminium, iron, copper, zinc, silver, tin, or lead, these metals show a decided anticatalytic effect, and that their oxides, hydroxides, and carbonates act in a similar manner; other examples of the action of catalyst poisons will be found in subsequent chapters. It will be observed that even minute traces of poisons may have disastrous effects, and therefore, for certain classes of reactions, it is essential to provide for the preparation of contact masses free from poisons or for the removal of such poisons from them, and also for the careful purification of the reacting substances.

The discovery of the anticatalytic effect of certain substances is of very great importance; equally important is the observation that other substances have a directly opposite influence. In many catalytic reactions it has been found that the addition of small quantities of " promoters " or " activators," as they are called, has the result of increasing the activity of catalysts in a very remarkable manner. This appears to be specially the case where the catalyst is a metal, and then the promoters may be other metals, or oxides, hydroxides or salts of the alkali metals, of the alkaline earth metals, and generally of those metals which yield oxides and salts which are not reducible by hydrogen: various other instances of the advantageous employment of promoters are given in the description of the synthesis of ammonia, of the oxidation of ammonia to nitric acid, and of other catalytic processes. The mode of action of promoters is not understood; indeed, our knowledge of the phenomenon is at present limited to some isolated facts, but there can be no doubt that further experimental investigation will lead to a more extended application of this method of activating catalysts.

In some cases where two catalysts are able to induce the same reaction the joint effect if they are used simultaneously

is the same as if each were acting alone, but very often the joint effect is not the sum of the separate effects but frequently greater. This is the case, for instance, when a mixture of copper sulphate and mercuric sulphate is used as the catalyst in the oxidation of naphthalene with sulphuric acid.

The number of substances known to be effective as catalysts in reactions of many different kinds is already very large, and grows continually as a result of the increasing attention given by chemists to this field of investigation. Probably there are very few, if any, substances which are not capable of exercising a catalytic influence of some kind on the progress of chemical change, but however that may be, it is certainly the case that many of the reactions carried out both in the laboratory and on the manufacturing scale are influenced, favourably or otherwise, by the presence in the materials undergoing the reaction of small quantities of foreign substances which have a catalytic effect.

Many of the catalysts employed in industrial chemistry are referred to in the following chapters, and, as will be seen, the list includes both non-metallic and metallic elements, acids and bases, oxides, chlorides and many other salts of both the commoner and the rarer metals, certain compounds of carbon, etc. The methods of preparing and applying many of these substances are indicated in the discussion of the processes in which they are used, and it is unnecessary to recapitulate the information given in these sections; at the same time it will be convenient to give at this stage a brief description of the methods of obtaining active forms of a few of the metallic catalysts in general use.

Nickel, iron, and copper have found extensive application as catalysts, usually when in a state of fine division, and for certain purposes their efficiency depends in a marked degree upon the method of preparation employed, since this determines not only the physical condition of the metal, but also its freedom from catalyst poisons.

Nickel prepared by reduction of the oxide with hydrogen at a bright red heat is almost inert as a catalytic agent;

on the other hand, when obtained by precipitating nickel hydroxide from a solution of the nitrate, washing and drying the precipitate and then reducing it at a temperature of about 250°, the metal is extremely active, but at the same time very sensitive to catalyst poisons. A generally useful form of the metal, which retains its activity for a long time, can be prepared by calcining the nitrate at a dull red heat and reducing the oxide thus obtained at about 280°. Since the presence of even minute traces of chlorine, and still more of bromine or iodine, in the metal paralyzes its catalytic power, an oxide obtained by precipitation from the chloride should not be used as a source of the metal; on the other hand, the oxide obtained by calcination of the sulphate frequently gives good results. An increased surface of the catalyst may be produced by depositing it on pumice; for example, by impregnating fragments with a solution of an easily reducible nickel salt, *e. g.* the formate, drying, and reducing with hydrogen, or by mixing the pumice with a paste of nickel hydroxide and water, drying and treating with hydrogen.

When used for processes of hydrogenation, etc., the oxide should be reduced in the same tube in which the process is carried out, in order that the activity of the reduced metal shall not be impaired by its contact with atmospheric oxygen.

An ingenious method which has been suggested for the production of a very pure and very finely divided form of the metal in contact with the substance under treatment, for example, a fat undergoing the hardening process, consists in converting the metal into nickel carbonyl, which when passed into the heated material breaks down into nickel and carbon monoxide.

The behaviour of a nickel catalyst towards poisons is said [1] to differ considerably according to its method of preparation. A catalyst prepared by distributing basic nickel carbonate on an inorganic carrier and reducing it at a temperature of 450° was found to be remarkably resistant

[1] Kelber, *Ber.*, 1916, **49**, 1868.

to poisoning by anticatalysts such as hydrocyanic acid, sulphuretted hydrogen, and carbon disulphide, and, for hydrogenation at the ordinary temperature, to have an activity much greater than that of nickel prepared by reduction at much lower temperatures. For hydrogenation in liquid media at the ordinary temperature it is recommended to prepare the nickel by precipitating the basic carbonate from a solution of the sulphate in presence of infusorial earth, washing and drying the precipitate, heating in hydrogen at 450° for two hours, allowing to cool in the current of hydrogen, and then passing a current of carbon dioxide over the catalyst for half an hour.

For certain purposes iron may be used in the form of powder or of fine wire without special purification, but in some cases, for instance in the synthesis of ammonia from nitrogen and hydrogen, the traces of impurities which are present even in the purest forms of commercial iron render it quite ineffective, or, at least, seriously impair its efficiency as a catalyst. The metal may be obtained in a state of purity by burning pure commercial iron in a current of oxygen and then reducing the magnetic oxide thus formed with carefully purified hydrogen, preferably at a temperature of about 450°.

Copper is often employed in the form of commercial copper powder, or is prepared in a very fine state of division by precipitation from a solution of the sulphate with zinc dust. For such purposes as the dehydrogenation of alcohol it is preferable to use copper obtained by reduction of its oxide at a comparatively low temperature. The metal in this form is a very useful catalyst, but its activity varies considerably according to the method of preparation. Copper oxide obtained by heating copper turnings in air or by calcination of the nitrate, when reduced with hydrogen at such a temperature that incandescence occurs, yields a form of the metal with rather low catalytic power, but when the metal is prepared by slow reduction at a temperature of 180°–200° of the finely divided oxide produced by addition of alkalis to boiling solutions of copper salts its catalytic

action is much more intense. An active form is also obtained by impregnating fragments of pumice with a solution of copper formate, drying, and reducing with hydrogen at as low a temperature as possible.

Platinum is sometimes used as a catalyst in the compact state or as spongy platinum, but, of course, is more active when finely divided (platinum black), and most of all when in colloidal solution.

A very active form of platinum black is prepared as follows.[1] A solution of 50 gr. of platinic chloride in 50–60 c.c. of water is mixed with 70 c.c. of a 40 per cent. solution of formaldehyde, the mixture well cooled, and 50 gr. of sodium hydroxide dissolved in an equal weight of water slowly added. After standing for twelve hours the precipitated metal is collected with the aid of the filter pump and washed with water until a deep black liquid begins to pass through. At this stage the washing is interrupted, and the precipitate left to stand for several hours, until it has assumed the form of a loose porous mass. It is then washed with water until every trace of sodium chloride has been removed, pressed in porous paper, and dried in a desiccator over sulphuric acid. Chlorides have a very deleterious effect on the catalyst, and must be completely eliminated.

Both platinum and palladium are very efficient catalysts in processes of hydrogenation when in the colloidal state. Colloidal solutions of these metals are not difficult to prepare, and may be kept for a considerable time, although not in the presence of some substances. Moreover, Paal has shown that their stability is considerably increased in the presence of certain organic substances. The substances originally used by Paal, to which he applied the names protalbic acid and lysalbic acid, may be prepared from egg albumin,[2] by heating at 100° with a 3 per cent. aqueous solution of sodium hydroxide for one hour. On acidifying the solution with acetic acid protalbic acid is precipitated, whilst lysalbic acid remains dissolved. The protalbic acid

[1] Loew, *Ber.*, 1890, **23**, 289. [2] *Ber.*, 1902, **35**, 2195.

is purified from salts by dialysis, washed with alcohol, and dried; it is a white powder, easily soluble in aqueous acetone or acetic acid, and in both acids and alkalis. Lysalbic acid is isolated by evaporating the mother liquor to small bulk and acidifying with sulphuric acid. It is then purified by pouring its concentrated aqueous solution into alcohol, and when dry forms a fine white powder, soluble in water.

An alkaline solution of sodium lysalbate or protalbate is treated with platinic chloride and a slight excess of hydrazine hydrate and left to stand for five hours. The salts produced are removed by dialysis and the solution concentrated, first on the water-bath and then in a vacuum. The product when dried at 100° forms black lustrous scales, which dissolve readily in water to a dark brown opalescent solution. Colloidal solutions of palladium may be prepared in a similar manner.[1] The solutions are very stable, and even when concentrated can be heated for some time without undergoing change.

The use of colloidal platinum and palladium has been greatly simplified by modifying the methods employed in the preparation of the catalyst. In place of lysalbic acid or protalbic acid gum arabic is now used as the protective colloid, and preliminary reduction of the metallic salt is not necessary. To the alcoholic solution of the substance to be reduced, aqueous (1 per cent.) solutions of palladium or platinum chloride and of gum arabic are added, care being taken that the solution remains clear, and hydrogen is then passed in either at the ordinary or at slightly increased pressure.[2] With unsaturated substances other than aldehydes or ketones the metal is as a rule precipitated in a granular form, and then hydrogenation is very slow, or does not take place at all; if, however, a trace of a previously prepared colloidal solution of the metal is added before passing in the hydrogen the metal then separates in the colloidal and not in the granular form, whatever the nature of the unsaturated compound present.[3]

[1] Paal, *Ber.*, 1902, **35**, 2195. [2] D. R. P. 230724.
[3] Skita and Meyer, *Ber.*, 1912, **45**, 3579, 3589.

In general, the most satisfactory method for the hydrogenation of unsaturated compounds, when in solution, is to add to the solution of platinum chloride and gum arabic a trace of a colloidal platinum or palladium solution, and then to pass in hydrogen; the unsaturated substance, which may be present from the beginning or added after reduction of the platinum salt, is then easily reduced by hydrogen.

Colloidal solutions of the metals may be prepared by passing hydrogen into previously warmed solutions of platinum or palladium chloride and gum arabic. If these solutions are dialysed and then evaporated to dryness in a vacuum colloidal platinum or palladium is obtained in the form of black scales which are readily soluble in water, and these are suitable for effecting hydrogenation in acid, alkaline, or neutral solution. These colloidal metal solutions are not decomposed even on boiling with acetic acid, and this forms the basis of a rapid method of hydrogenating aromatic or heterocyclic compounds. A small quantity of a colloidal solution of platinum or palladium is added to a homogeneous solution in acetic acid of the substance to be reduced, platinum chloride, and gum arabic, and the whole is shaken with hydrogen until the theoretical quantity has been absorbed.

Solutions of palladious chloride and of potassium chloroplatinite containing gum arabic when treated with sodium carbonate give palladious and platinous hydroxides in a colloidal condition; careful evaporation in a vacuum after dialysis leaves the colloidal hydroxide in the form of brown or black scales respectively, which readily dissolve in water again. Solutions of these hydroxides when shaken with hydrogen are reduced, and on evaporation scales of the colloidal metal are left. The colloidal hydroxides themselves are well suited to reduction processes.[1]

In the present state of our knowledge of catalytic phenomena, it is not possible to say beforehand what catalyst will be most effective in promoting a given reaction. It is

[1] Skita and Meyer, *loc. cit.*

known, of course, that different groups of catalysts are specially suitable for purposes of oxidation, reduction, hydrogenation, dehydration, etc., and to that extent some guidance in the choice of a catalyst will be afforded by consideration of the nature of the reaction which it is desired to promote. But although general considerations of this kind will assist the chemist by preventing him from spending time in testing the action of substances which will almost certainly prove to be ineffective, yet the ways of catalytic agents are so bewildering in their diversity that as a rule, much careful experimental work will be required in each case before the most efficient agent is discovered. Of course in such investigations it is of vital importance to ensure the absence of all substances which may act as catalyst poisons, and in this connection it must not be forgotten, when reactions in solution are concerned, that the course of the change may be greatly modified, catalytically or otherwise, by the nature of the solvent. Thus it has been found that in the preparation of bromo-derivatives of aromatic hydrocarbons an ionizing solvent such as nitrobenzene assists substitution in the nucleus, whilst non-ionizing solvents, for example, carbon disulphide and carbon tetrachloride, have the effect of promoting substitution in the side chain. Again, in experiments on the hydrogenation of unsaturated substances in solution, using palladium-nickel as catalyst, benzene has been proved to have a marked inhibiting effect, which persists even after the catalyst has been thoroughly washed with ether and gently heated in hydrogen; a similar effect is produced by acetone, whilst alcohol and ether have no such action. Another subject, regarding which very little is known at present, will repay careful study, namely, the remarkably beneficial effects produced by admixture of suitable promoters with catalysts.

CHAPTER II

Hydrogen

Within the last twenty years the technical applications of hydrogen have greatly increased in both number and importance. The gas is now used in very large quantities in a number of chemical manufactures; for example, the synthesis of ammonia from its elements, the hydrogenation of oils, and the reduction of many organic compounds; also for the production of the high temperatures required in such operations as the fusion and welding of platinum and the manufacture of apparatus from fused silica; for the final treatment of the tungsten filaments used in electric lamps, which are heated to a high temperature in an inert atmosphere, usually a mixture of hydrogen and nitrogen; for filling balloons and dirigible air-craft. Moreover, it is essential that the hydrogen used for many of these purposes should be free from even traces of oxygen or of impurities such as carbon monoxide, acids, or volatile compounds of sulphur, phosphorus or arsenic.

The large and increasing demand for pure hydrogen has naturally led to the investigation of methods by which the gas can be prepared and purified economically, and many different processes have been patented; a number of these involve the use of catalysts.

A whole group of patents is based on the fact that in presence of suitable catalysts, steam and carbon monoxide interact, at moderately high temperatures, with the formation of hydrogen and carbon dioxide: $H_2O + CO = H_2 + CO_2$. Of course, water gas, or other mixtures of gases containing carbon monoxide, may be used instead of the pure monoxide.

In this group the patent [1] of Mond and Langer is of

[1] Eng. P. 12608 (1888).

historic interest. Mond found that when carbon monoxide or gaseous hydrocarbons are brought into contact with nickel at temperatures between 350° and 400°, or with cobalt at slightly higher temperatures, decomposition takes place into carbon and carbon dioxide or hydrogen respectively, the carbon combining with the metal. If steam be now introduced at a moderate temperature this carbon reacts with it to form hydrogen and carbon dioxide. These reactions take place simultaneously when mixtures of carbon monoxide and steam, or of hydrocarbons and steam, are passed through the apparatus, the ultimate products in each case being hydrogen and carbon dioxide. The catalyst is prepared by saturating pieces of pumice stone with a solution of the chloride of nickel or of cobalt, drying, and reducing with hydrogen.

As examples of more recent patents the following may be quoted. Water gas mixed with steam is passed at a temperature exceeding 400°–500° over a catalyst such as oxide of iron, and the carbon dioxide produced is removed by means of lime.[1] Carbon monoxide and steam are caused to interact at 300°–600°, under a pressure of from 4 to 40 atmospheres, in the presence of a catalyst, such as iron, nickel, or the like, the carbon dioxide produced being removed by absorption.[2] In a modification[3] of this process, oxygen or air is passed into the contact chamber in addition to the carbon monoxide and steam. The oxygen combines with part of the hydrogen, and the combustion generates sufficient heat to render the process continuous, whilst the steam which is formed takes part in the reaction and serves to reduce the quantity needed from an external source. According to another patent,[4] water gas or other gas containing carbon monoxide is passed with an excess of steam over heated finely divided metals of the iron group, especially iron, cobalt, or nickel, or their oxides. The catalyst is best prepared by the addition of appropriate diluents or binding agents, organic or inorganic, which may be such as to give

[1] Fr. P. 375164.
[2] Eng. P. 26770 (1912).
[3] *Ibid.* 27117 (1912).
[4] Fr. P. 459918.

off gas on heating so as to increase the porosity. For example, dry precipitated ferrous carbonate may be made into a plastic mass with lime, water, caustic potash and ferric nitrate, and the mixture dried and heated to 500°. A reaction temperature of preferably not over 600° is maintained by adjusting the temperature of the gases before they enter the contact chamber. In a First Addition (1914) to this patent it is claimed that contact masses composed of metals or oxides of metals other than iron, cobalt and nickel may be used, together with "activating" substances consisting of compounds of metals differing greatly in chemical properties, such as basicity, stability, etc., from the metal used as catalyst. It is also claimed [1] that when contact masses are used containing such activating substances, especially the oxygen compounds of chromium, thorium, uranium, glucinum, antimony, and the like, the reaction is practically quantitative at a relatively low temperature: the contact mass should not be heated above 600° during preparation or use. Small quantities of carbon monoxide may be readily removed from gaseous mixtures with the aid of the contact masses described. The use of a catalyst consisting of spathic iron ore or hydroxide iron ores has also been protected: the contact mass may be made into lumps by means of aluminium hydroxide or other binding agent, and must not be heated above 650°, either during the reaction or beforehand.[2]

In the manufacture of hydrogen by the interaction of steam and carbon monoxide or gases containing it, there is a risk that methane may be formed when nickel is used as the catalyst. In order to obviate this risk, whilst at the same time retaining satisfactory activity of the catalyst, it has been proposed [3] to use a contact mass containing in addition to nickel or its oxides a preponderating quantity of iron or its oxides.

Recently it has been claimed [4] that a maximum yield of hydrogen can be obtained by passing steam and carbon

[1] D. R. P. 279582.
[2] Eng. P. 16494 (1914).
[3] D. R. P 282849.
[4] Eng. P. 6477 (1914).

monoxide over catalysts consisting of or containing metallic couples. A suitable iron-copper couple may be made by heating iron oxide with sodium carbonate, washing the product with water in order to remove the caustic alkali which is formed, reducing the iron oxide with hydrogen, cooling, moistening the reduction product with copper nitrate solution and then heating it in a current of hydrogen. Carbon monoxide mixed with an excess of steam is passed over the resulting couple, which is heated to a temperature of 500°. A silver-iron couple is also said to be very effective. A related patent [1] covers the use of a catalyst containing a "lixiviated alkali ferrite," prepared, for example, by roasting a mixture of sodium carbonate and burnt pyrites at about 1000°, and lixiviating with hot water in order to recover the greater part of the caustic alkali formed.

In certain other patented processes,[2] the interaction of steam and carbon monoxide is effected through the catalytic action of heated lime or of a mixture of lime with other materials (*e. g.* 5 per cent. of iron powder), with the advantage that the carbon dioxide is fixed as it is produced :

$$H_2O + CO + CaO = H_2 + CaCO_3.$$

The elimination of the carbon dioxide is said to be very complete. Modifications [3] of the original process cover the use of pressure and the employment of carbon, in the form of lignite or of wood charcoal, along with alkali or alkaline earth oxides or hydroxides. It is stated that with lime a temperature of from 600° to 800° is required, but that baryta or alkalis may be used at a lower temperature, and that if the process is conducted on similar lines to the manufacture of water gas, but with the employment of a mixture of lime and charcoal, almost pure hydrogen is obtained by working with steam at a pressure of 10 atmospheres. A very similar process is described in a later patent.[4] A mixture of a gas containing carbon monoxide, but free from nitrogen, with steam in the proportion of

[1] Eng. P. 6476 (1914).
[2] *Ibid.* 13049 (1912).
[3] D. R. P. 284816.
[4] U.S. P. 1173417.

1 volume of the monoxide to 4–5 volumes of steam is passed over a mixture of caustic lime and a catalyst at a temperature of from 500° to 550°. The catalyst, *e. g.* a metallic oxide, forms 5 per cent. of the mixture and the gases and the heated mass come into contact on the counter-current principle. Under these conditions the carbon monoxide is converted into the dioxide and forms calcium carbonate; the hydrogen is collected and dried.

In still another process [1] a mixture of "hydrocarbons" and steam is employed. The mixed gases are passed over an inactive refractory oxide, such as magnesia, which is covered with a catalyst, *e. g.* nickel or nickel oxide, and heated to a temperature of from 800° to 1000°. The resulting gaseous mixture is freed from carbon monoxide and carbon dioxide, leaving substantially pure hydrogen.

An entirely different method for the production of hydrogen is facilitated by the catalytic action of various substances, although not dependent upon it. Some chemical reactions can be promoted by the application of high pressures, whereby it is possible to retain one or more of the reacting substances in the liquid state from the boiling point to the critical point, and so to utilize the physical properties of liquids at high temperatures and to cause reactions to take place which cannot be carried out at low temperatures. Moreover, the properties of a liquid may undergo remarkable changes between the boiling point and the critical point; thus according to Noyes the electrolytic dissociation of water increases between these points nearly two thousandfold. This suggests that water at high temperatures, provided that it is kept in the liquid state, should act as a fairly strong acid or base, and in the presence of a suitable metal should enter into reaction with evolution of hydrogen. Guided by these ideas Bergius [2] has worked out a method for producing hydrogen by the action of liquid water, heated above its boiling point, on iron in a closed

[1] Fr. P. 463114.
[2] *J. Soc. Chem. Ind.*, 1913, **32**, 462; D. R. P. 254593; D. R. P. 286961.

vessel capable of withstanding high pressures. The reaction is carried on at a temperature of from 300° to 340°, and takes place quantitatively: $3Fe + 4H_2O = 4H_2 + Fe_3O_4$. The speed of the reaction increases with increase of temperature, and is also affected favourably by the presence of small quantities of such substances as sodium chloride, ferrous chloride, etc., or of a metal such as copper, which act as catalysts. This is shown clearly by the following figures:—

	Temperature.	Quantity of hydrogen per hour.
Iron and pure water . . .	300°	230 c.c.
Iron and pure water + $FeCl_2$ . .	300°	1390 c.c.
Iron and pure water + $FeCl_2$ + Cu.	300°	1930 c.c.
Iron and pure water + $FeCl_2$ + Cu.	340°	3450 c.c.

Within the limits practically attainable, the speed of the reaction is stated to be so great that in a vessel of 10 gallons capacity about 3000 cub. ft. of hydrogen per day may be generated. The gas obtained is extremely pure, because the carbon and sulphur compounds in the iron are practically not attacked by the liquid water. The hydrogen is obtained under high pressure (up to 300 atmospheres) and may be directly filled into cylinders without previous compression.

Still another method depends upon the reaction between steam and heated carbon, which under certain conditions results in the formation of hydrogen and carbon dioxide: $2H_2O + C = 2H_2 + CO_2$. This can be effected[1] by causing liquid water at a high temperature to act on carbon in presence of a catalyst soluble in water. For example, 100 kilos of coke and 200 kilos of water containing in solution 1 kilo of thallium chloride are placed in a strong iron vessel provided with a valve, and the vessel is heated to a temperature of 360°. The mixture of hydrogen and carbon dioxide which collects in the upper part of the vessel is blown off at intervals of half an hour and the carbon dioxide is

[1] D. R. P. 259030.

absorbed by lime. Under the conditions described a daily production of 5 cub. metres of hydrogen is possible.

Hydrogen produced by the interaction of steam and carbon monoxide invariably contains small quantities of the latter compound, which is a specific poison for certain catalysts and must consequently be removed. This may be effected by treatment with calcium carbide or by compression on to heated soda-lime; for the removal of traces of carbon monoxide it is also recommended that the hydrogen should be brought into contact with solutions of caustic alkalis at high temperatures and pressures; *e. g.* hydrogen containing 1 per cent. of carbon monoxide can be treated with 80 per cent. sodium hydroxide at 260° and 50 atmospheres pressure, or with 25 per cent. sodium hydroxide at 240° under a pressure of 200 atmospheres.[1]

Chlorine

It is possible to oxidize hydrochloric acid directly by means of oxygen; but the two gases interact so slowly, even when heated, that in order to make the reaction available for the preparation of chlorine its velocity must be increased through the influence of a catalyst. For this purpose copper salts have proved most suitable, although other substances are capable of producing a similar catalytic effect. When a mixture of hydrochloric acid and air is passed over heated cuprous chloride, the following change takes place:—

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O.$$

Upon this reaction the well-known Deacon process is based.

As indicated in the equation, the reaction is reversible, and at the most favourable working temperature the oxidation of the hydrochloric acid is by no means complete; any unchanged acid is, however, easily recovered and used again. The action of the catalyst is supposed to take place in stages: first an oxychloride of copper is formed, this in turn reacts with the hydrochloric acid to form cupric chloride and water, and finally the cupric chloride is decomposed at the

[1] Fr. P. 439262.

temperature of the apparatus into cuprous chloride and chlorine :—

(1) $4CuCl + O_2 = 2Cu_2OCl_2$;
(2) $2Cu_2OCl_2 + 4HCl = 4CuCl_2 + 2H_2O$;
(3) $4CuCl_2 = 4CuCl + 2Cl_2$.

The reaction between hydrochloric acid and oxygen is exothermic ($2HCl + O = Cl_2 + H_2O + 14700$ cal.) and therefore whilst at moderate temperatures the reaction proceeds from left to right, increase of temperature tends to promote the reverse reaction. Thus it has been shown that when the ordinary mixture of hydrochloric acid and air is used, at 430° from 75 to 80 per cent. of the acid is oxidized, whereas at 577° rather less than 50 per cent. is transformed into chlorine. Consequently, the lower the temperature the greater the quantity of hydrochloric acid oxidized. The temperature, however, cannot be reduced below a certain point because otherwise the reaction would become extremely slow, even in presence of a catalyst, and it is not practical to carry out the process at temperatures below 400°–430°. At 450° equilibrium is more rapidly attained, but the yield of chlorine is diminished, and moreover at temperatures much above 400° appreciable quantities of the catalyst are lost through volatilization.

In the original form of the Deacon process the hydrochloric acid, mixed with air, was led directly from the salt-cake furnace into the contact apparatus. The hydrochloric acid was thus apt to be contaminated with sulphuric acid, ferric chloride and arsenic, the catalyst was very soon spoiled by these impurities, and consequently the yield of chlorine rapidly diminished. The process did not become successful until it was realized that in order to prevent rapid deterioration of the catalyst the hydrochloric acid must be freed from impurities. The first method which was adopted with this end in view is as follows : The gas coming from the salt-cake furnace is absorbed in water, and from the concentrated solution of hydrochloric acid thus obtained a regular stream of the pure gas is liberated by allowing concentrated

sulphuric acid to flow in, finishing up by blowing in air. The hydrochloric acid mixed with the proper amount of air is then passed into the contact chamber, whilst the dilute sulphuric acid is concentrated for use over again. More recently the process has been restored to its original simplicity by obtaining from mechanical salt-cake furnaces a mixture of hydrochloric acid and air containing about 30 per cent. by volume of the acid, which is freed from dust and sulphuric acid by passing it through a series of water-cooled condensers, and then heated to 220° and directly passed into the contact apparatus where, owing to the heat evolved in the reaction, a temperature of 400°–450° prevails.

The yield of chlorine depends greatly on the proportions in which hydrochloric acid and air are present in the mixture of gases, and on the velocity of the current of the gases. The best results are obtained when the mixture contains not more than 20 per cent. of hydrochloric acid. The mixture of gases finally produced contains only from 8 to 12 per cent. of chlorine, but is quite suitable for making bleaching powder in the special apparatus designed for the purpose.

Another catalytic process for the manufacture of chlorine, and simultaneously of sodium sulphate, consists in passing a mixture of dry sulphur dioxide and air over heated sodium chloride, which is mixed with clay in order to prevent fusion and with a catalyst, such as ferric oxide or cupric oxide, which promotes the reaction :—

$$4\,NaCl + 2SO_2 + O_2 = 2Na_2SO_4 + 2Cl_2.$$

Hargreaves and Robinson [1] were apparently the first to observe that this reaction could be effected in presence of a small quantity of a catalyst. They suggest as a suitable proportion 1 lb. of Cu, in the form of a copper salt, per ton of sodium chloride, and claim the use of copper, manganese, and chromium, and the salts of those metals, as catalysts.

Conroy [2] has found that salt is decomposed by a mixture of sulphur dioxide and air to yield sodium sulphate and chlorine at a temperature below 600°, but that in absence

[1] Eng. P. 828 (1873). [2] *J. Soc. Chem. Ind.*, 1902, **21**, 302.

of a catalyst the reaction is very slow. With the addition of 0·25 per cent. of copper to the salt, reaction begins at 400°, and becomes more rapid with rise of temperature, the velocity at 600° being about 50 per cent. greater than at 450°. Increase of the percentage of copper also increases the rate of reaction; about 0·5 per cent. of iron has much the same effect as half that quantity of copper. With a suitable speed of the current of gas all the sulphur dioxide is retained by the salt whilst its equivalent of chlorine is liberated: at higher speeds both sulphur dioxide and chlorine escape. It was found that the conversion of the chloride into the sulphate of sodium could be made complete. In this reaction the probable effect of the catalyst is to induce the combination of the sulphur dioxide with oxygen: the sulphur trioxide thus produced will react with the salt, in presence of excess of oxygen, to form sodium sulphate.

A recent patent [1] describes a continuous process for the preparation of chlorine and sodium sulphate from common salt. A mixture of the latter with a catalyst, for example ferric oxide, is subjected to the action of sulphur dioxide and oxygen at a temperature of about 600° in a horizontal cylindrical rotary chamber.

Hydrochloric Acid

Large quantities of both hydrogen and chlorine are liberated in electrolytic alkali works, and various proposals have been made for the production of hydrochloric acid from these elements. One at least of these processes [2] claims the use of a catalyst, in this case charcoal. It is stated that combination of hydrogen and chlorine to form hydrochloric acid is brought about continuously, quietly, and without danger by passing a mixture of the gases in molecular proportions over coarsely pulverized charcoal, the temperature being regulated by means of a water-bath.

[1] U.S. P. 1255020.

[2] Eng. P. 1831 (1900).

Hypochlorites and Chlorates

Hypochlorites and chlorates of the alkali metals are now prepared by electrolysis of aqueous solutions of the corresponding alkali chloride, one salt or the other being obtained according to the conditions under which the process is carried out. In each case the addition to the solution of a small quantity of potassium chromate, about 1 gr. per litre, which prevents cathodic reduction of the product, produces a marked increase in the yield. For example, with a neutral 30 per cent. solution of sodium chloride the yield of active oxygen (from the hypochlorite) was only 32·8 per cent., the reduction being 54·5 per cent.; with addition of 0·18 per cent. of K_2CrO_4 to the solution these figures became 69·6 per cent. and 3·6 per cent. respectively.

The effect of the catalyst is to be ascribed to a partial reduction of the chromate and the formation of a thin deposit of chromium chromate round the cathode, which prevents contact of the bulk of the liquid with the cathode and thus with nascent hydrogen.

Other catalysts than potassium chromate have been recommended, among those being vanadium salts, sodium resinate, and certain organic sulphur compounds in presence of calcium salts.[1]

The addition of a chromate is equally effective in the electrolytic preparation of bromates and iodates, and enables a current efficiency of over 90 per cent. to be obtained.

Graphite

The production of graphite from coke or anthracite on the manufacturing scale was successfully worked out by Acheson,[2] to whom the possibility of the process was suggested by his previous work on carborundum (CSi). When a mixture of sand and coke is heated to a high temperature in an electric furnace, the carborundum produced is found to be surrounded by a certain quantity of graphite. Investigation

[1] D. R. P. 141372, 205087. [2] U.S. P. 568523.

showed that this graphite had been produced by decomposition of some of the carborundum, and that the conversion of amorphous carbon into graphite does not require the presence of sufficient silica to combine with all the carbon, but that a far smaller quantity is effective. Moreover, other oxides than silica, for example, ferric oxide, aluminium oxide, and boric oxide, are also active to varying degrees in bringing about the transformation: within certain limits the greater the quantity of oxide present the lower the temperature at which the reaction begins.

The action of these oxides is undoubtedly catalytic, and the most probable explanation of their mode of action is to be found in the assumption that carbides are formed as intermediate products. When, at the high temperature of the furnace, the oxide has been reduced by the carbon the liberated metal forms a carbide, which subsequently decomposes, giving graphite. The metal then combines with more of the amorphous carbon, and the process continues until all the carbon present has been converted into graphite, when the metal volatilizes away. This explanation is supported by the fact that after all the amorphous carbon has been converted into graphite the charge can be almost completely freed from impurities by further heating.

Graphite is produced by this process either in the form of powder or as finished articles such as lamp carbons, electrodes, crucibles, etc. In making the finest qualities of lubricating graphite the raw material used is petroleum coke, which is mixed with from 1 to 2 per cent. of ferric oxide as catalyst. Lower qualities are made from anthracite ground to small particles: in this case the silica, alumina, and ferric oxide naturally present in the anthracite are sufficient in quantity to catalyse the reaction. For the preparation of graphite articles such as electrodes, finely powdered petroleum coke is used, which is compressed and moulded with the aid of some tar or pitch, the requisite quantity of a suitable oxide being added as catalyst. When placed in the furnace the objects are surrounded and separated from each other by layers of granulated coke, which

ensures the gradual and regular heating which is necessary in order that the gases may escape from the interior of the articles without damaging them.

The furnace used has permanent end walls and arrangement of electrodes, a shallow bed of fire-brick, and movable side walls of carborundum bricks. A layer of carborundum is placed on the bed to protect it from fusion, then the charge is filled in to the lower edge of the electrodes, then a conducting core of graphite, and finally more charge is heaped around and above the core, and the whole covered with a layer of siloxicon, a very refractory greyish-green powder always obtained in the manufacture of carborundum. The duration of a run is 20–24 hours, and during this period a 1000 H.P. furnace will convert 90 per cent. of a six-ton charge into graphite.

For making graphite electrodes and rods another method has also been used. The moulded article, to which boric oxide has been added as catalyst, is drawn by rollers through a horizontal arc passing between carbon electrodes in a closed chamber filled with an indifferent gas. This treatment graphitizes the articles sufficiently for some purposes.

Carbon Tetrachloride

At the ordinary temperature chlorine has little or no action on carbon disulphide, but if the latter contains a catalyst, or " chlorine carrier," such as iodine, antimony pentachloride, etc., a rapid reaction occurs which results in the formation of carbon tetrachloride and sulphur monochloride :—

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

Dry chlorine is passed into carbon disulphide containing from 2 to 12 per cent. of iodine in solution; when the reaction is completed the products can be separated from each other by fractional distillation or by other known methods. Bromine or pentachloride of antimony may replace the iodine, but are said to be less efficacious.[1]

The sulphur monochloride produced in this reaction can

[1] Eng. P. 18990 (1889).

be caused to react with carbon disulphide in presence of a catalyst with formation of carbon tetrachloride and sulphur : $CS_2 + 2S_2Cl_2 = CCl_4 + 6S$. The catalyst employed is a metal or metallic halide, preferably iron or ferric chloride. Excess of the chloride of sulphur is used, because then the reaction is rendered less violent and the yield is improved. The mixture of carbon disulphide and sulphur monochloride, with addition of the catalyst, is heated to about 60°, at which temperature the reaction begins, and when it is completed the liquid is heated to boiling for a short time. On cooling the sulphur separates in crystals; the liquid is fractionally distilled in order to separate the carbon tetrachloride from the excess of chloride of sulphur, and the crude tetrachloride is purified.[1]

Carbon tetrachloride can also be prepared from carbonyl chloride by passing the latter gas through a series of towers containing a substance such as coke, bone charcoal or pumice, which by contact action induce the decomposition of the carbonyl chloride into carbon dioxide and carbon tetrachloride : $2COCl_2 = CO_2 + CCl_4$. The latter compound is condensed in a worm cooled by water.[2]

Carbonyl Chloride

Carbon monoxide and chlorine unite to form carbonyl chloride ($CO + Cl_2 = COCl_2$) when a mixture of the gases, containing preferably a slight excess of chlorine, is exposed to sunlight, but the combination can be caused to take place even in the dark by passing a mixture of equal volumes of the gases through a tube containing heated animal charcoal, which acts as a catalyst.

Removal of Carbon Disulphide from Coal Gas

The sulphur compounds which still persist in coal gas after removal of the sulphuretted hydrogen consist mainly of carbon disulphide, the proportion by volume of this impurity

[1] Eng. P. 19628 (1893). [2] U.S.P. 808100.

being about 0·02 per cent. of the gas. In view of the very large quantities of gas to be dealt with in large works and of the very small concentration of the carbon disulphide in the gas, a reaction of high velocity should be used for its elimination. It is well known that if coal gas be heated to about 500° most of the sulphur compounds are converted into sulphuretted hydrogen, the carbon disulphide reacting with the hydrogen in the gas to form hydrogen sulphide and carbon: $CS_2 + 2H_2 = 2H_2S + C$. In presence of suitable catalysts the velocity of the reaction is greatly accelerated; moreover, under such conditions the reaction is not reversible and the decomposition of the carbon disulphide is complete.

From 1906 onwards numerous experiments were conducted, under Carpenter's direction,[1] on the relative efficiency of different catalysts under various conditions, and, for work on the large scale, nickel in a fine state of division was found to be the most satisfactory. The activity of the catalyst was soon destroyed owing to deposition of carbon on its surface, but the carbon could easily be removed and the nickel regenerated by heating in a current of air. In order to permit of the use of a relatively small contact surface and at the same time to effect the reaction with high velocity, it was found desirable that the temperature of the catalyst should be as high as could be employed without consequent deterioration of the quality of the gas, as regards calorific and illuminating value, and of the durability of the container. A large number of experiments showed that the most suitable temperature was 450°–500°; an essential feature of the process is the preheating of the gas before it enters the tubes containing the catalyst, otherwise such a furnace temperature is required to maintain the catalyst at the requisite temperature that the tubes are speedily destroyed. In order to prevent the intense local heating which occurs during aeration of the catalyst for removal of the carbon when the metal is used alone, the contact mass is made of a highly porous fireclay impregnated with nickel

[1] Carpenter, *J. Gas Lighting*, 1914, **126**, 928; Evans, *J. Soc. Chem. Ind.*, 1915, **34**, 9.

reduced from the chloride. The presence of sulphuretted hydrogen decreases the efficiency of the catalyst, hence the process cannot be advantageously applied to crude gas.

The plant now installed at East Greenwich Gas Works consists of five units, each capable of dealing with three million cubic feet of gas per day. Each unit has a producer and a combustion chamber, on each side of which are heating chambers which contain the reaction tubes. The gas, freed from sulphuretted hydrogen, flows into the heat interchangers, which are filled with three-inch steel tubes, and then in parallel currents through the reaction tubes. After passing over the catalyst the hot gas flows through the heat interchangers in a contrary direction to the incoming gas, to which it gives up a large proportion of its heat, and finally through the secondary purification vessels for removal of the sulphuretted hydrogen. The gas is preheated to about 400°, and the reaction takes place at 450°. When a particular unit is shut down for the purpose of burning off the carbon which is deposited on the nickel, the coal gas contained in it is displaced by chimney gas, and then air in regulated quantities is driven through by a fan. When the combustion of the carbon is complete the residual air is in turn swept out by chimney gas, and the plant is then again ready for use. The total weight of nickel in this plant is 1321 lb.

Grillet [1] has proposed another process for the purification of gas by heat which is based upon the reaction which takes place between carbon disulphide and steam, in presence of oxide of iron, with the formation of carbon dioxide and sulphuretted hydrogen: $CS_2 + 2H_2O = CO_2 + 2H_2S$.

This reaction is hardly perceptible at the ordinary temperature and in absence of the catalyst, but in its presence even at as low a temperature as 130° more than 67 per cent. of the carbon disulphide contained in the gas is said to be converted into sulphuretted hydrogen. For the reaction to be complete it is necessary that the sulphuretted hydrogen produced be continually absorbed, and an admirable material

[1] *Soc. Tech. de l'Industrie du Gaz en France*, 1912, 245.

for the purpose exists in oxide of iron as used in gas purifiers. The crude gas is already saturated with water vapour, and all that is necessary is to raise it to a suitable temperature and pass it through a purifier containing heated oxide of iron.

SULPHUR

Recovery of Sulphur from Alkali Waste.[1]

When alkali waste is treated with carbon dioxide according to Chance's well-known process, a mixture of gases consisting chiefly of nitrogen and containing 25 per cent. or less of sulphuretted hydrogen is obtained. This sulphuretted hydrogen is converted into sulphur by limited oxidation by means of air with the aid of a catalyst. The operation is carried out in a special form of kiln (the Claus kiln), the mixture of gases being passed through a particular form of oxide of iron, or of disulphide of iron produced from this in the course of the process, which also has a catalytic effect: the necessary temperature is maintained by the heat of reaction.

It is possible that when the working temperature is reached the reaction would proceed equally well whatever the catalytic material used. Thus according to Forbes Carpenter[2] broken brick is stated to be used successfully in place of oxide of iron if the temperature of the kiln be maintained high enough. Whether that be the case or not, it is certain that the catalyst plays an important part when a new and cold kiln is being started.

Manganese dioxide may be used as catalyst in place of ferric oxide; it is active at a lower temperature than ferric oxide in effecting the reaction ($2H_2S + O_2 = 2H_2O + 2S$), and at that lower temperature there is less liability to the counter action. Forbes Carpenter recommends the use of Weldon mud as catalyst, placed as a layer some inches thick on the top of the filling of iron ore usually provided.

Within the limits of effective reaction the efficiency of

[1] Conroy, *J. Soc. Chem. Ind.*, 1902, **21**, 305.
[2] *36th Annual Report on Alkali Works* (1900).

the kiln is determined by the temperature of the contact material rather than by the proportions of air and of sulphuretted hydrogen in the reacting mixture or by the rate of flow of the mixture through the kiln. With respect to the most favourable conditions for maximum decomposition of the sulphuretted hydrogen, accompanied by the highest yield of free sulphur, Carpenter and Linder [1] have arrived at the following conclusions: (1) The temperature of the catalyst should not fall below 200°; a higher temperature results in the oxidation of the sulphur formed to sulphur dioxide, especially if excess of air is present. With manganese dioxide as catalyst, at temperatures below 200° the reaction is characterized by formation of free sulphur, but above 260° by formation of sulphur dioxide; with ferric oxide as catalyst the reactions on the whole are characterized by the formation of sulphur dioxide rather than of free sulphur; with broken brick the reaction on the whole is characterized by the large amount of sulphuretted hydrogen escaping unoxidized, and by formation of free sulphur rather than of sulphur dioxide. (2) The proportion by volume of air present in the reaction mixture should not exceed from 3·5 to 4 times that of the sulphuretted hydrogen. (Theoretically, 1 volume of sulphuretted hydrogen requires 2·5 volumes of air for oxidation to sulphur.) (3) The rate of flow of the reacting mixture of gases should not much exceed 0·75 cub. foot per minute per sq. foot of superficies.

The reaction in the Claus kiln is far from complete, a state of equilibrium, varying with the temperature, being reached between the sulphuretted hydrogen, sulphur dioxide, oxygen, and steam. From 15 to 20 per cent. of the sulphur may escape from the sulphur chambers in the form of sulphuretted hydrogen and sulphur dioxide.

Sulphuric Acid. The Chamber Process

The manufacture of sulphuric acid by the chamber process consists essentially in the oxidation of sulphurous acid, or

[1] *J. Soc. Chem. Ind.*, 1903, **22**, 457.

of sulphur dioxide in presence of water, with atmospheric oxygen through the catalytic agency of oxides of nitrogen. In the presence of the catalyst the reaction proceeds with great rapidity, but otherwise its completion requires a long time.

This important manufacturing process has been described so often and in such detail that any account of it would be superfluous. At the same time attention may be directed to the rather remarkable fact that, although this classic example of catalysis has been studied by many chemists, there is even yet difference of opinion as to the actual part played by the catalyst in promoting the oxidation of sulphurous acid. It is recognized that the oxides of nitrogen act as oxygen carriers, but the mechanism of the process has received several different interpretations.

One of the oldest explanations is represented by the following equations :—

(1) $SO_2 + H_2O = H_2SO_3$;
(2) $H_2SO_3 + NO_2 = H_2SO_4 + NO$;
(3) $2NO + O_2 = 2NO_2$.

Lunge,[1] on the other hand, expressed the view that the greater part of the sulphuric acid is formed by two successive reactions, of which the first yields an unstable compound, nitrosyl sulphuric acid, which is decomposed by water in the second :—

(1) $2SO_2 + H_2O + O_2 + N_2O_3 = 2(NO)HSO_4$;
(2) $2(NO)HSO_4 + H_2O = 2H_2SO_4 + N_2O_3$.

Raschig[2] supposes that an unstable compound, nitrososulphonic acid, is first formed by the action of sulphur dioxide on nitrous acid, and is at once transformed by more nitrous acid, with loss of nitric oxide, into another unstable compound, nitrosisulphonic acid, which in turn breaks down into sulphuric acid and nitric oxide :—

(1) $HNO_2 + SO_2 = (NO)SO_3H$;
(2) $(NO)SO_3H + HNO_2 = (NH)SO_5H + NO$;
(3) $(NH)SO_5H = H_2SO_4 + NO$.

[1] Cf. Divers, *J. Soc. Chem. Ind.*, 1904, **23**, 1178.
[2] *J. Soc. Chem. Ind.*, 1911, **30**, 166.

Recently Reynolds and Taylor [1] have come to the conclusion that Raschig's views are not supported by the results of experiment; that it must be regarded as doubtful if nitrosyl-sulphuric acid plays any important part in the exchanges in the chamber, and that the first of the explanations just referred to substantially represents the course of the reaction.

A recent patent [2] covers what appears to be a valuable method of controlling the working of sulphuric acid plant in the chamber process. According to this patent the gas, free from oxides of nitrogen, entering the acid-making system, and also the gases containing nitrogen oxides at a predetermined point near the Glover tower, where the percentage of sulphur dioxide is normally more than 0·7 per cent. by volume, are analysed, and by regulating the amounts of sulphur dioxide and of oxides of nitrogen introduced into the system, the ratio between the percentages of sulphur dioxide in the gases at the two points is maintained at the value found best adapted to a commercially complete absorption of the oxides of nitrogen.

In an account of this system of control [3] Fairlie points out that the largest single item of expense in operating a sulphuric acid chamber plant is nitrate of soda, and that the most important of the inventions designed to effect a saving in the consumption of that substance is, of course, the Gay Lussac tower, in which oxides of nitrogen escaping from the last chamber are recovered. The efficiency of the tower depends largely upon the way the process is handled, and most of all upon the careful introduction of just that amount of oxides of nitrogen required for the oxidation of the sulphur dioxide admitted to the chamber.

In order to obtain the best results in the Gay Lussac tower a certain ratio must be maintained between the percentage of sulphur dioxide in the chamber gases at some point near the front end of the chamber system and the percentage of

[1] *J. Soc. Chem. Ind.*, 1912, **31**, 367.
[2] U.S. P. 1205723.
[3] *J. Soc. Chem. Ind.*, 1917, **36**, 196.

sulphur dioxide in the gases from the pyrites burners before admixture with nitrous fumes. What the desirable ratio is must be determined for every possible grade of burner gas (by an analytical method [1] modified from that of Reich). An increase in the ratio above what is desirable indicates the need of more nitrate, a decrease is a sign that the quantity of nitrate must be reduced.

The oxides of nitrogen are recovered most completely in the Gay Lussac tower when the proportions of nitric oxide and nitric peroxide in the gases entering the tower are exactly those required for the formation of nitrous anhydride ($NO + NO_2 \rightleftharpoons N_2O_3$). A small quantity of sulphur dioxide is needed in the gases entering the tower, for otherwise an excess of nitric peroxide above the quantity required to combine with the nitric oxide will be present, and this excess will be lost, since nitric peroxide is only slightly soluble in the cold 78 per cent. sulphuric acid with which the tower is charged.[2] On the other hand, if there is too much sulphur dioxide in the gases entering the tower, an excess of nitric oxide will be present, and this also will be largely lost. It has been demonstrated that the proportions of nitric oxide and nitric peroxide will be correct when the percentage of sulphur dioxide in the gases as they pass into the Gay Lussac tower is between 0·07 and 0·10 in cold weather, and between 0·09 and 0·12 in moderate or warm weather. Careless handling of the process at the front of the system will be plainly indicated by testing the gas at the entrance to the Gay Lussac tower.

This analytical method of controlling the working of the chamber system is claimed to be particularly valuable in starting up a set of chambers after a shut down or in setting a new plant in operation for the first time, when it frequently happens that a period of experimentation, varying in duration from days to months, elapses before the working of the chambers becomes regular. In such cases this method of control indicates what is wrong and what remedy must be applied.

[1] U.S. P. 1205724.

[2] According to Lunge vapours of nitrogen peroxide are quickly and completely absorbed by 78 per cent. sulphuric acid.

Sulphuric Acid. The Contact Process

In 1831 a process was patented by Phillips for the production of sulphuric anhydride from sulphur dioxide and oxygen through the catalytic action of platinum. The sulphur dioxide mixed with a suitable proportion of air was pumped through heated tubes of platinum or of porcelain containing platinum wire and sponge; the issuing gases were passed into large sandstone towers, lined with lead and filled with pieces of quartz, down which water or dilute acid trickled, the acid collected at the bottom being pumped up to the top of the tower to meet fresh quantities of gas.

From 1875 onwards fuming sulphuric acid was manufactured by a catalytic method at Freiberg and in London, where Squire and Messel succeeded in placing on a commercial footing a process which they patented in that year. According to this process, sulphur dioxide and oxygen in equivalent proportions were obtained by causing the vapour of concentrated sulphuric acid to pass over a highly heated surface, when decomposition of the acid ensues :—

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

The mixture of sulphur dioxide and oxygen, dried by passage through concentrated sulphuric acid, was passed over spongy platinum, either alone or distributed over some porous substance, at a low red heat, and the sulphuric anhydride produced was either condensed in a suitable apparatus or else absorbed by concentrated sulphuric acid.

In this process the reacting substances were used in the proportions required by the equation $2SO_2 + O_2 \rightleftharpoons 2SO_3$, and for long the erroneous belief was held that successful results could only be obtained by close adherence to these proportions. It was not recognized that the reaction is reversible, and no application was made of the law of mass action, according to which the proportion of dioxide converted into trioxide of sulphur should be greater the larger the excess of oxygen present. Hence, although it gradually became evident that highly diluted sulphur dioxide, such as

the mixture of gases from pyrites burners, could be used with success, patents for the technical production of contact sulphuric acid were not taken out until 1898. The ultimate success of the process was largely due to the work of Knietsch and his collaborators; the difficulties encountered in its technical development are outlined in a lecture given by Knietsch to the German Chemical Society,[1] from which the following summary is mainly derived.

Preliminary experiments with sulphur dioxide largely diluted with air proved that its conversion into the trioxide was practically complete when platinum was used as the catalyst, even great dilution in no way hindering the reaction. Platinum, in the form of platinized asbestos, was the most effective of all the catalysts of which trial was made, being active even at the low temperature of 400°. Further experiments were made with the gases from pyrites burners, led to the laboratory through a long leaden pipe which acted as a settler for dust, and further purified by passage through concentrated sulphuric acid, with equally satisfactory results, and moreover the activity of the catalyst remained unimpaired even after long use. Experiments on the large scale were then undertaken, but although the gases from the burners were purified in exactly the same way, and in addition were passed through dry coke and asbestos filters, yet the activity of the catalyst gradually diminished to zero. Investigation proved that certain substances, especially arsenic, exercise a poisonous effect on platinum, even very small amounts sufficing to destroy its catalytic activity, and arsenic was found in the white cloud of sulphuric acid which is always present in the gases even after the purifying treatment described. The necessity for thorough purification of the gases was thus established, but to effect this proved to be one of the most difficult problems in the development of the process; to achieve success the most thorough and intimate mixture of the gases with water or with sulphuric acid is necessary, and must be continued until optical as well as chemical purity is reached. The gases should be

[1] *Ber.*, 1901, **34**, 4069; *J. Soc. Chem. Ind.*, 1902, **21**, 172.

slowly cooled, otherwise the sulphuric acid cloud is much more difficult to remove by the subsequent treatment. At first long iron pipes were used for this purpose, but in spite of the purity of the gases slow but sure deterioration of the catalyst occurred; this effect was finally traced to the presence of arsenic in a gaseous form, proceeding without doubt from the action of the acid on the iron, since when contact between them was prevented this deterioration was no longer observed. When the pyrites burners were being worked hard a cloud of sulphur containing arsenic often appeared, which resisted all attempts to remove it and which seriously affected the catalyst. The formation of this cloud was finally prevented by blowing in steam so as to effect thorough admixture of the hot gases, with consequent complete combustion of the sulphur. Several collateral advantages followed; the acid present was diluted and condensed so that it did not reach the iron or lead pipes, and the formation of hard crusts of flue dust in the pipes was very much reduced.

It was known that the combination of sulphur dioxide with oxygen is exothermic ($SO_2 + O = SO_3 +$ 22600 cal.), yet originally this fact received little attention, and the earlier forms of contact apparatus were so arranged as to be raised to a red heat and maintained at that temperature by external heating, whereas, in fact, the reaction once started, cooling instead of heating is necessary. Progress has been made in this direction so as either to use the purified gases from the burners for cooling purposes and thus to heat them directly, or to utilize the heat of the gases coming from the contact chamber. In these circumstances the reaction is almost quantitative at the atmospheric pressure; no compression of the gases is necessary, as was thought to be the case in the early days.

The packing of the platinized asbestos is a matter of some importance. It must not be so loose that the gases can pass through without contact, nor so close as to offer great resistance to the passage of the gases. A suitable arrangement is that of layers of asbestos on perforated plates kept

at a little distance from each other; in this way all the tubes of the apparatus can be similarly and evenly packed.

For the absorption of the sulphuric anhydride produced oil of vitriol containing 97–98 per cent. of sulphuric acid is much more effective than either water or sulphuric acid of any other strength. In practice a single absorption vessel is sufficient for even a rapid current of gas provided that the strength of the absorbing acid be kept uniform by the regulated addition of water. At this particular concentration of sulphuric acid the boiling point is at the maximum, and the vapour pressure at the minimum; the specific gravity is also at the maximum, and the electric resistance suddenly begins to rise at this point towards a maximum with 100 per cent. acid; moreover, the action on iron is considerably less than with other concentrations.

When fuming sulphuric acid is to be made, more than one absorbing vessel may be needed. Cast iron is unsuitable for such vessels, not because it is readily attacked, but because it is liable to fracture or explode. This appears to arise from slow diffusion of the fuming acid into the iron, with consequent gradual evolution of sulphur dioxide and sulphuretted hydrogen, thus causing a state of internal stress. Wrought iron is attacked by fuming acid containing less than 27 per cent. of sulphuric anhydride, but when the content of anhydride exceeds this the acid has practically no action, and vessels of wrought iron may be used for years without sensible corrosion.

In the reaction between sulphur dioxide and oxygen, of course, the law of mass action holds, so that the complete conversion of the sulphur dioxide into sulphuric anhydride is impossible with the reacting gases mixed in the exact theoretical proportion; this can only be effected by having an excess of oxygen present. If chamber gases are used (containing, say, 7 volumes of sulphur dioxide, 10 volumes of oxygen, and 83 volumes of nitrogen) the nitrogen is without influence except that it affects the velocity of the reaction. The limit of the reaction is dependent solely upon the temperature, and not upon the nature of the catalyst.

At temperatures below 200° there is no reaction, whilst at 900°–1000° sulphuric anhydride is dissociated into sulphur dioxide and oxygen; between these limits the reaction occurs, reaching a maximum at about 450°. Hence in order to increase the velocity of the reaction as much as possible a catalyst which has its greatest activity at about 450° should be used; the catalyst which best fulfils this condition is platinum.

Platinum, although probably the best, is not the only catalyst which can be utilized in the manufacture of sulphuric acid. Another process in operation is based upon the power possessed by oxides of iron and other metals of promoting the combination of sulphur dioxide and oxygen at a moderate red heat.[1] Ferric oxide (pyrites cinder), obtained by the roasting of pyrites, which has been allowed to grow cold has only feeble catalytic power, but if it be used fresh and if the air for the combustion of the pyrites be dried previous to admission to the burners, a conversion of 60 per cent. of the sulphur dioxide into sulphuric anhydride is readily obtained, and the proportion converted may under suitable conditions rise to 90 per cent. The reaction is said to proceed more completely if the furnace gases, which usually contain from 6 to 8 per cent. of sulphur dioxide, are diluted to a content of from 2 to 3 per cent. of the dioxide by means of dried and heated air before admission to the contact chamber.[2]

The contact ovens are placed in the centre of a block of pyrites burners. Heated air is admitted below the grates of the burners and the hot gases pass directly from these through the contact mass, maintaining it at the red heat necessary for the reaction. Preliminary purification of the gases is unnecessary, and notwithstanding this a comparatively pure product is obtained, for the catalyst whilst effecting the conversion at the same time fixes most of the arsenic in the form of a non-volatile compound with the oxide of iron. The activity of the catalyst is reduced as the quantity of arsenic abstracted by it increases, but this is not a serious

[1] Eng. P. 17266 (1898). [2] *Ibid.* 3185 (1899).

difficulty, since the contact mass is easily replaced by fresh material always at hand.[1]

It is doubtful whether a complete conversion of the dioxide into the trioxide of sulphur can be brought about on the technical scale with ferric oxide alone, since according to Knietsch's figures the temperature necessary with this catalyst lies so high as to bring about dissociation of some of the trioxide. Indeed, this difficulty is indicated in a later patent,[2] which proposes to overcome it by combining the ferric oxide and the platinum processes. According to this modification of the original method the partially converted and purified gases issuing from the ferric oxide chamber are passed through a dry scrubber and then through a second chamber containing platinum. Another patent [3] claims the use of other metallic oxides as well as ferric oxide.

More recently the use of vanadic acid precipitated on finely ground pumice or a similar carrier has been protected, and two methods of preparing the catalyst are given. According to the first,[4] a mixture of 200 parts of moist pumice stone in powder and 14 parts of ammonium vanadate is moulded to the desired shape, and heated at a temperature of 300° to expel ammonia and then at 440° in gases containing sulphur dioxide to promote cohesion. Alternatively a complex insoluble compound containing one or more easily replaceable bases, *e.g.* permutite, is treated with a salt of vanadium, and the salt reduced in hydrogen.[5] Still later patents [6] claim the use of catalysts composed of (1) an intimate mixture of voluminous active chromium sesquioxide and an oxygen compound of an easily fusible heavy metal which is capable of absorbing sulphur dioxide and acts as a binding material for the chromic oxide but does not combine with it, (2) a mixture of the chromic oxide and tin oxide, one of them being in excess of the amount required for the formation of tin chromate, and one of them being catalytically active, or

[1] Eng. P. 1859 (1899).
[2] *Ibid.* 24748 (1899).
[3] *Ibid.* 4610 (1901).
[4] *Ibid.* 23541 (1913).
[5] *Ibid.* 8462 (1914).
[6] U.S. P. 1204141, 1204142, and 1204143.

(3) a porous mixture of chromic oxide and an activating agent, which may be obtained, for example, by heating together a mixture of ammonium dichromate and tin chloride, or a mixture of the oxides of chromium and tin with an organic substance.

Persulphuric Acid and Persulphates

The persulphates of the alkali metals, and particularly the ammonium salt, are now largely used as oxidizing agents and in photography, and persulphuric acid itself is employed to a constantly increasing extent as a source of hydrogen peroxide, which is produced by hydrolysis of the acid:—

$$\begin{array}{cc} HOH & O{\cdot}SO_2OH \\ HOH & O{\cdot}SO_2OH \end{array} + \begin{array}{cc} & \\ | & | \\ & \end{array} = \begin{array}{cc} HO & HO{\cdot}SO_2OH \\ HO & HO{\cdot}SO_2OH. \end{array}$$

The sulphates, *e.g.* ammonium or potassium sulphate, are converted into persulphates by electrolytic oxidation under suitable conditions. The anode compartment contains a saturated solution of the sulphate, and the cathode compartment sulphuric acid of medium strength; the electrolyte is well cooled, since the temperature is best kept at about 15°. It has been found that certain catalysts exercise a very favourable influence on the oxidation, and that the chloride and fluoride ions are particularly active.

The same catalysts promote the formation of persulphuric acid. By electrolysis of sulphuric acid in presence of hydrochloric or hydrofluoric acid solutions of persulphuric acid containing up to 40 per cent. of that compound are obtained, which when distilled under reduced pressure yield hydrogen peroxide, formed by hydrolysis of the persulphuric acid.

Sulphuryl Chloride

Sulphur dioxide and chlorine do not readily unite to form sulphuryl chloride under ordinary conditions, but the combination is easily effected in presence of catalysts:—

$$SO_2 + Cl_2 = SO_2Cl_2.$$

According to a patented process for the production of

sulphuryl chloride,[1] sulphur dioxide and chlorine, in the liquid state, are caused to react with each other in presence of substances which promote their union, such as camphor, glacial acetic acid, anhydrous formic acid, etc. For example, camphor is dissolved in liquid sulphur dioxide in a closed vessel and a stream of liquid chlorine in calculated quantity is introduced, preferably while cooling. The product is purified by distillation.

Production of Chromic Acid by Electrolytic Oxidation of Chromium Salts

Solutions in which chromic acid or dichromates of the alkali metals, together with sulphuric acid, have been used as oxidizing agents contain chromium sulphate formed by reduction of the chromic acid; the chromic acid can be regenerated from the chromium sulphate by a process of electrolytic oxidation.

The best solution for the purpose contains 100 gr. of chromic oxide (as sulphate) and 350 gr. of sulphuric acid per litre. With a lead anode a current efficiency of 100 per cent. can be obtained, whereas with an anode of platinum no oxidation takes place.

It has been found that the addition of small quantities, from 1 per cent. down to 0·1 per cent., of various substances has a marked effect in improving the efficiency of the process. Among these substances are potassium fluoride, potassium cyanide, sodium phosphate, boric acid, sodium vanadate, and sodium molybdate; their action is, of course, catalytic, but the mechanism is not understood.

[1] Eng. P. 12861 (1901).

CHAPTER III

Ammonia

It is primarily due to the pioneer work of Haber and Le Rossignol [1] that the synthesis of ammonia from its elements, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, has now become an industrial operation of the first importance. The Haber process was first commercially installed in Germany by the Badische Anilin- und Soda-Fabrik in 1913, with a plant capable of producing 30,000 tons of ammonium sulphate per annum; apparently the output in that year was some 20,000 tons. This grew to 60,000 tons in 1914, to 150,000 tons in 1915, and to 300,000 tons in 1916, and it is stated with authority that the output in 1917 was equivalent to at least 500,000 tons of ammonium sulphate.

The affinity of nitrogen for hydrogen is so small that the gases do not unite to any appreciable extent at the ordinary temperature or even when heated. The combination of nitrogen with hydrogen is an exothermic reaction, hence it is only due to lack of reaction velocity that the gases do not combine at the ordinary temperature. The velocity of the reaction increases rapidly as the temperature is raised, but, as will be seen from the following table, the yield of ammonia falls. The best mixture of nitrogen and hydrogen for the production of ammonia has the theoretical value, one volume of nitrogen : three volumes of hydrogen, but even with this most favourable mixture the percentage of ammonia obtainable under ordinary pressure is very small at high temperatures. Increase of pressure, of course, favours the formation of ammonia, since the combination of nitrogen and hydrogen results in a diminution in the number of molecules from

[1] *Zeit. Elektrochem.*, 1913, **19**, 53; Haber, *J. Soc. Chem. Ind.*, 1914, **33**, 49.

four to two, and therefore the percentage of ammonia in equilibrium attainable is proportional to the working pressure over a very wide range. Reference to the table shows that the values for the percentage equilibrium at high pressures are very different from those at the ordinary pressure, and technical synthesis of ammonia becomes a possibility if the equilibrium at such high pressures can be reached in a short enough time.

PERCENTAGE AMOUNT OF NH_3 IN THE EQUILIBRIUM OF THE REACTION $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

Temperature . . .	550°	650°	750°	850°	950°
Pressure, 1 atmos.	0·0769	0·0321	0·0159	0·0089	0·0055
Pressure, 100 atmos.	6·7	3·02	1·54	0·874	0·542
Pressure, 200 atmos.	11·9	5·71	2·99	1·68	1·07

The figures show that in order to obtain results of technical value in the synthesis of ammonia a catalyst is required which will have a satisfactory effect in promoting the velocity of the reaction at a temperature not much above 500°. The upper limit of temperature for practical working is 700°; at higher temperatures any advantages arising from increased reaction velocity are more than counterbalanced by the falling off in the yield of ammonia. In no case is the yield so high that it would prove remunerative to absorb the ammonia from the reaction products and allow the residual hydrogen and nitrogen to go to waste, hence a continuous process must be adopted in which the residual gases, after removal of the ammonia, are again passed over the catalyst. The simplest method of separating the ammonia is liquefaction by cooling, temperatures down to − 73° being used; below this point there is a risk of solidification of the ammonia leading to stoppages.

With suitable catalysts it is possible to work at temperatures between 500° and 600° and at high pressures so that the equilibrium is nearly maintained with a high rate of flow of the gases. The very high pressure limits the space which may be filled with the catalyst, but more than 1 kilo of ammonia per hour is easily produced for each litre of catalyser

space. The necessary heat is produced by the reaction itself, for within the stated range of temperature 13,000 calories are liberated by the formation of one gramme equivalent of ammonia from its elements.

Details of working methods have not been published, but a general idea of the arrangement of plant can be formed from the descriptions of the large-scale experimental plant used by Haber,[1] and from the following patent.[2]

The catalyst, for example finely divided iron, is contained in a metal tube, which at one end communicates with a heat exchanger and at the other receives the mixture of nitrogen and hydrogen. The gases pass over the heated catalyst and through the heat exchanger, and then the cooled gases traverse either an absorption apparatus or a refrigerator in which the ammonia is condensed. The gases are finally made to return by means of a pump along the outside of the heat interchanging tubes and of the tube containing the catalyst, to re-enter the latter and be circulated afresh, the supply of gases being replenished as required through a side tube. The apparatus is surrounded by heat insulating material, and is enclosed in an envelope to enable the circulation to be effected under pressure.

The process, whatever its exact details may be, is, of course, not free from danger, since at the high pressures employed very small quantities of oxygen entering the apparatus suffice to cause explosions. This risk is guarded against by setting up the apparatus in bomb-proof chambers.

An extensive study has been made of the various catalysts which may be used in the synthesis of ammonia, and numerous patents [3] indicate the wide range of materials available for this purpose. It is understood that the catalyst now in use on the manufacturing scale is iron, in a fine state of division, which has been rendered very active by addition

[1] *J. Soc. Chem. Ind.*, 1913, **32**, 134.

[2] Fr. P. 406943.

[3] *e.g.* D. R. P. 235421; D. R. P. 238450; Eng. P. 17951 (1909); Eng. P. 26749 (1911); Eng. P. 61 (1911); Eng. P. 5855 (1911); Eng. P. 3345 (1912).

of a small amount of a "promoter," but many other substances have been tested. Osmium in a very fine state of division was found by Haber to be a highly effective catalyst; with this metal, at a temperature of about 550° and a working pressure of 175 atmospheres a yield of about 8 per cent. by volume of ammonia was readily obtained. For use on the large scale, however, osmium can hardly be considered seriously because of its scarcity. Uranium is also very efficient especially when used in the form of its carbide; this in the current of hydrogen and nitrogen is converted into the nitride of uranium, which is a powder of very high catalytic power. It is essential when uranium is used that no water or substance which can give rise to water is present in the mixture of gases. Molybdenum and its compounds, such as molybdic acid, ammonium molybdate, and the compound of molybdenum and nitrogen which is obtained by heating molybdic acid or ammonium molybdate in a current of pure ammonia, are excellent catalysts. So also is manganese provided that the mixture of hydrogen and nitrogen is completely free from oxygen or water. Another suitable substance is tungsten, either the metal itself or an alloy or a nitrogen compound of the metal; the catalyst should be prepared at a temperature not greatly exceeding 600°, or by heating a tungsten compound in ammonia, in which case a higher temperature may be employed if necessary. Other metals may be employed with good results, the list including the alkali metals, the alkaline earth metals, or rare metals such as cerium, niobium, tantalum, etc. and others again of a more complex character, of which the following may be mentioned. The catalyst contains a metal or a metallic compound with a considerable power of taking up nitrogen and also one with a similar tendency to combine with hydrogen. For example, ammonium molybdate is heated till part of the ammonia is expelled, and the porous grains thus produced are soaked in a concentrated solution of palladium nitrate (which may contain 2 per cent. of uranium nitrate), 20 per cent. of the salt relative to the weight of ammonium molybdate being employed: the mixture is calcined until the

nitrate is decomposed, and then reduced with hydrogen. Or, again, the catalyst consists of asbestos, meerschaum, etc., soaked in a solution of an alkali osmate or ruthenate and dried, or the catalyst is prepared by treating a complex insoluble compound containing one or more easily replaceable bases, *e.g.* permutite, with a salt of a catalytic metal such as palladium, copper, nickel, or vanadium, and reducing the salt with hydrogen.

Various modifications of the original process of Haber have been patented, for instance, passing the nitrogen and hydrogen over the catalyst alternately instead of simultaneously; it is stated that in this case specially good results are obtained by mixing the nitrogen with from 1 to 3 per cent. of hydrogen. A current of nitrogen containing a small quantity of hydrogen is passed into a vessel containing the catalyst, *e.g.* lithium-manganese nitride, which is heated to a temperature of from 450° to 550°, until a pressure of about 50 atmospheres is attained; absorption is allowed to proceed until the pressure has fallen to, say, 30 atmospheres, the nitrogen is then removed and hydrogen passed over the mixture preferably at about 50 atmospheres pressure and at the same temperature. In all cases it is claimed that the yield of ammonia is increased by depriving the gaseous mixture of water and of substances capable of forming water; this can be suitably effected by passage over heated palladium asbestos and then over quicklime.

In the course of the study of the various catalysts the important observation was made that a number of substances have the power of rendering catalysts in general more active, and that in many cases very small quantities of these "promoters" or "activators" are sufficient to raise the catalytic activity in a marked degree. Among these promoters are the oxides, hydroxides, and salts of the alkali, alkaline earth and earth metals, oxides of the rare earth metals tantalum and niobium, silica, and a number of other substances, including many metals themselves. As a general rule those metals which yield oxides and salts which are not reducible by hydrogen, and compounds of such metals, are

suitable for use as promoters.[1] For example, powdered iron mixed with 5 per cent. of aluminium borate or phosphate is stated to give a satisfactory yield of ammonia at 500° or 450° respectively; or, again, cerium prepared electrolytically in the form of small grains is mixed with about two per cent. of potassium nitrate and placed in the contact tube; when a mixture of hydrogen and nitrogen is passed through the heated tube a catalyst is obtained which gives about three times the yield of ammonia that untreated cerium affords.

Another very important result of the study of methods for the synthesis of ammonia was the recognition of the fact that certain substances are specific " poisons " for ammonia catalysts, that is to say, are fatal to their activity. The most injurious substances are sulphur, selenium, tellurium, phosphorus, arsenic, antimony and boron, or compounds of these elements such as their hydrides. Sulphur dioxide is very poisonous and carbon monoxide is also a poison. Metals of low melting point, which can easily be formed from their compounds by reduction with hydrogen, such as lead, zinc, bismuth, and tin must also be avoided. Extremely minute quantities of these substances which are almost always present even in the purest commercial products, or in so-called pure gases, suffice to render the catalysts absolutely inactive or at least to diminish their activity very seriously. Thus iron, for example, prepared from ordinary iron oxide with a content of one per thousand of sodium sulphate is as a rule inactive; iron containing 0·1 per cent. of sulphur is generally quite useless and even with 0·01 per cent. is of very little use, although in appearance and when examined with the ordinary physical and chemical methods no difference at all can be detected when it is compared with pure iron.[2] A trace of sulphur, one part per million, in the mixture of gases can under certain conditions be injurious so that even electrolytically prepared hydrogen must generally be subjected to further special purification.

[1] Fr. P. 425099; D. R. P. 276133; U.S. P. 1068968.
[2] Haber, *J. Soc. Chem. Ind.*, 1912, **31**, 982.

The recognition of these facts necessitates the preparation of catalysts free from such poisons, and also the very careful purification of both the hydrogen and the nitrogen. Various processes with this end in view have been protected by patents. For example, pure commercial iron containing a trace of sulphur is burned in a current of oxygen, and the resulting magnetic oxide is reduced to the metal.[1] Again, it is suggested to pass the mixture of gases through two separate quantities of the catalyst, the first to absorb any poison the gases may contain, and the second serving for the actual catalysis, or to use purifying tubes containing substances which will absorb the poisons.[2]

An interesting account has been given by Maxted[3] of the efforts made by a British company towards the establishment of the synthetic ammonia industry in this country on a technically sound basis. He states that the methods in existence for the direct production of a hydrogen-nitrogen mixture tend to give a gas containing appreciable quantities of carbon monoxide, which is a catalyst poison, and therefore it is more satisfactory from an economic standpoint to manufacture the pure gases separately and mix them in proper proportions as required. It is advantageous to work at as high a pressure as is compatible with the strength of the materials used in the plant, but in practice it is not possible to much exceed 200 atmospheres, and 180 atmospheres is found to be a very suitable working pressure.

The available catalysts, apart from the metals of the platinum group, are uranium and iron. The former is decidedly the more efficient, but has the drawback of being prepared and regenerated with difficulty and of being rapidly rendered inactive by traces of water or of oxygen in the gases. For this reason it is preferable to employ iron containing traces of other substances as promoters, using two or even more promoters simultaneously.

The following table gives the actual percentage of ammonia obtained with an iron-potash catalyst. The third

[1] Fr. P. 429696. [2] Eng. P. 5855 (1911).
[3] *J. Soc. Chem. Ind.*, 1917, **36**, 777.

column gives the yield provided that the ammonia formed is completely removed in the course of circulation, a condition which may be very nearly approached by employing a refrigerator almost at the solidifying point of ammonia ($-77°$), with a rate of circulation such that the percentage of ammonia in the gases is not too low. The temperature was, as usual, not uniform throughout the column of catalyst, but ranged from about 650° at the beginning of the column to about 600° at its end.

Time of contact with catalyst.	Percentage of NH_3 in gas.	Yield of NH_3 in kilos per hour per cub. ft. of catalyst space.
13 seconds . .	0·8	6·46
26 ,, . .	1·4	3·03
66 ,, . .	2·7	2·33
105 ,, . .	3·1	1·78
18 minutes . .	3·7	0·89

The most economical rate of working is not necessarily that at which the highest yield of ammonia per hour is obtained, but is modified by the efficiency of the heat and cold exchangers and by the completeness of the separation in the refrigerator of the ammonia formed.

For the economic efficiency of the process too great care cannot be given to the construction of the exchangers connected with the heated reaction vessel and the refrigerator respectively. This is obvious when it is considered that the cost of operating the process, apart from the compression of the gases, consists in supplying or abstracting sufficient heat to compensate for losses by radiation and for the deficiencies of the exchangers.

The maximum temperature is determined by the ammonia content of the gas mixture and by the pressure at which the process is being worked: it is necessary to remove the ammonia as completely as possible in the refrigerator. The following figures give the percentages of ammonia theoretically left in a mixture at 150 and 200 atmospheres respectively after passing through a refrigerator at different temperatures.

Temperature.	150 Atmospheres.	200 Atmospheres.
0°	2·7	2·1
— 10°	1·9	1·4
— 20°	1·2	0·9
— 30°	0·76	0·57
— 40°	0·47	0·35
— 50°	0·25	0·19
— 60°	0·13	0·1

The construction of the contact chamber presents considerable difficulty, firstly on account of the high pressure together with a temperature approaching a red heat, and specially on account of the rapid deterioration of the walls of the vessel through the action of the gases at high temperatures. In order to reduce this undesirable effect to a minimum the reaction vessel may be constructed of a material as resistant as possible to the action of ammonia and surrounded by a jacket of nitrogen at the same pressure as the gaseous mixture in the chamber, the whole being enclosed by a wall capable of withstanding the pressure.

The choice of a method of heating the apparatus is not easy. Electric heating presents drawbacks in practice, and therefore in Germany a system is adopted according to which air is injected into the catalyst chamber so that the requisite temperature is maintained by internal combustion. The method makes it possible to use chambers of simple construction, but is somewhat liable to give rise to explosions. If, as a result of too low a temperature in the chamber, or for other reasons, any of the oxygen remains unconsumed, it may accumulate until an explosive mixture results.

In a Report on the Nitrogen Industry to the War Department, U.S.A.,[1] Parsons states that during the past four years the General Chemical Company, working on the basis that it should be possible to develop conditions under which the synthetic formation of ammonia by the direct combination of hydrogen and nitrogen should take place at lower pressures than those deemed necessary by the Haber

[1] *J. Ind. and Eng. Chem.*, 1917, **9**, 839.

patent, have achieved success. The process has been in successful operation on a large experimental scale with several smaller units and with one unit supposed to be larger than those in use in Germany.

No account of this process has been published, but, judging by the claims made in a number of patents, apparently it has been found possible to bring about the combination of hydrogen and nitrogen at lower pressures by the use of specially active catalysts. According to one [1] of these, nitrogen and hydrogen, in the volume ratio of 1 to 3 are brought, under a pressure of from 34 to 95 atmospheres, into contact with a catalyst which consists essentially of an alkali metal and nitrogen, and which is heated to a temperature of from 550° to 600°. The gases must be purified from catalyst poisons. The yield of ammonia, which depends upon the gaseous pressure, is about 5 per cent. by volume. The catalyst is prepared [2] by heating purified ignited granules of pumice stone with metallic sodium in a neutral atmosphere so that the metal is melted and by vigorous stirring is caused to distribute itself uniformly in the pores of the pumice stone. The material is then heated in ammonia gas at about 300° until a constant weight is attained. Alternatively [3] the sodium, prior to being heated in ammonia is treated with a cobalt compound, and water soluble matter is removed from the product. A suitable catalyst can also be prepared [4] by reducing nickel oxide with hydrogen, adding sodium, and treating the mixture with ammonia.

It has also been claimed that a very marked increase in the yield of ammonia can be attained under less troublesome working conditions than those of the Haber patent by the use of catalysts prepared from alkali or alkaline earth ferrocyanides or ferricyanides by heating them at a temperature below 500°, and under pressure, in a current of nitrogen and hydrogen or of one of those gases. In presence of these catalysts the combination of nitrogen

[1] U.S. P. 1151537.
[2] *Ibid.* 1159364.
[3] *Ibid.* 1159365.
[4] *Ibid.* 1143366.

and hydrogen is said to take place at relatively low temperatures and pressures and the yield of ammonia to amount to no less than 17 per cent. by volume.[1]

Aluminium Nitride

A number of methods for the indirect preparation of ammonia from nitrogen have been proposed, which depend upon the production of various nitrides, *e. g.* the nitride of titanium, followed by the liberation of ammonia from these compounds through the action of water or of steam. One such process, due to Serpek, is understood to be on trial on the large scale in France in the works of the Société Générale des Nitrures.

Serpek's process is based upon the formation of aluminium nitride by heating a mixture of alumina and carbon to redness in a current of nitrogen,

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO,$$

and the subsequent decomposition of the nitride with water or with aqueous solutions of alkalis :—

$$AlN + 3H_2O = Al(OH)_3 + NH_3.$$

By treatment of the nitride with a solution of caustic soda or of sodium aluminate the nitrogen is liberated in the form of ammonia, whilst a very pure alumina suitable for the manufacture of aluminium is also obtained.

The first stage of this process may be classed among catalytic reactions, inasmuch as it has been proved that the absorption of the nitrogen, which is strongly endothermic and only takes place with rapidity at high temperatures, preferably from 1800° to 1900°, is greatly facilitated by the presence in the alumina of small quantities of powdered metals such as copper, aluminium, iron, or their alloys,[2] or of metallic oxides, hydroxides, or carbonates ;[3] the presence of free or combined sulphur in the alumina is also beneficial,

[1] D. R. P. 286719. [2] Eng. P. 7507 (1909).
[3] *Ibid.* 8349 (1912).

the reaction being accelerated and the quantity of nitride in the product increased.[1] Hence bauxite can be used with advantage instead of pure alumina, because owing to the catalytic effect of the impurities, such as ferric oxide and silica, present in the mineral, the formation of nitride can be effected more rapidly and at somewhat lower temperatures. It is also stated[2] that if varying proportions of free or combined hydrogen are added to the nitrogen the yield of nitride greatly exceeds that which would be obtained in the absence of hydrogen; a suitable way of generating nascent hydrogen at the temperature of the reaction is provided by the addition of a hydrocarbon or of sulphuretted hydrogen to the nitrogen.

The formation of aluminium nitride is likewise found[3] to be greatly accelerated by the presence of the oxides of certain elements which themselves can form stable nitrides. Under these conditions it is possible to secure rapidly and at a relatively low temperature a fairly high percentage of nitrogen in the product. Among the oxides which may be used are those of silicon, titanium, zirconium, chromium, molybdenum, tungsten, uranium, and glucinum. Preference is given to silica on account of its cheapness, but under certain local conditions others might be used with advantage, especially as they are recovered and can be utilized again. The oxides may be replaced by other oxygen compounds such as silicates, titanates, vanadates, etc. The presence of iron and other impurities does not influence the catalytic action, so that low grade bauxite may be employed. For example, bauxite, kaolin, clay, or any other substance containing mixtures or compounds of silica and alumina is heated with carbon in a current of nitrogen at a temperature between 1300° and 1500° for a sufficient time to convert almost all the silica into nitride, and then at 1700°–1800° for the formation of aluminium nitride. In the first stage of the process the nitrogen must contain no oxygen, free or combined, but in the second stage

[1] Fr. P. 426868. [2] Eng. P. 8348 (1912).
[3] D. R. P. 243839.

producer gas, freed from oxygen and carbon dioxide, may be used.[1]

Calcium Cyanamide

Calcium cyanamide, which is now used in very large quantity as a fertilizer ("Nitrolim"), and as a source of ammonia and of cyanides,

$$CaN{\cdot}CN + 3H_2O = CaCO_3 + 2NH_3,$$
$$CaN{\cdot}CN + C + Na_2CO_3 = CaCO_3 + 2NaCN,$$

is manufactured by heating calcium carbide in a current of nitrogen: $CaC_2 + N_2 = CaN{\cdot}CN + C$. The reaction is strongly exothermic, but appreciable absorption of nitrogen does not begin until the temperature is raised to about 700° when commercial carbide is used.

Under technical conditions, with large quantities of carbide, the heat liberated during the initial stages of the absorption serves to raise the temperature of the charge to 1000°–1100°, the temperature necessary for satisfactory absorption. External heating is required only for raising the charge to the initial reaction temperature and for compensating subsequent losses of heat. It has been found that various substances admixed with the carbide are capable of lowering the initial reaction temperature, and their technical use has been proposed. The best known of these substances are the chloride and the fluoride of calcium, but a large number of other compounds have been proved thus to facilitate the reaction. Such are lime (always present in the technical carbide), the carbonates of calcium, sodium, and potassium, the chlorides of lithium, sodium, and aluminium, etc.; calcium chloride appears to be the most efficient, as shown by the following results obtained by Bredig. In each experiment a sample of carbide was heated at 800° for two hours in a stream of nitrogen.

[1] Eng. P. 25141 (1911).

Addition.	Per cent. nitrogen absorbed.
—	3·2
10 per cent. lime	4·0
„ „ sodium carbonate	8·5
„ „ sodium chloride	13
„ „ calcium chloride	22

The effect of the quantity of the substance added is very irregular in the initial stages of the absorption, but in some cases these differences disappear in course of time, the tendency being for a constant percentage of the carbide to be converted into cyanamide, whatever the quantity of the addition; this only determines the velocity of the absorption of the nitrogen.

Sodamide

Sodamide, NH_2Na, is now a substance of technical importance, as it is used in very considerable quantity in place of sodium itself in various manufacturing operations, for example as a condensing agent in the preparation of synthetic indigo.

The formation of sodamide and other alkali amides by the interaction of ammonia and the alkali metals,

$$2NH_3 + 2Na = 2NH_2Na + H_2,$$

is greatly influenced by the presence of catalysts.[1] Whereas silicon, calcium carbide, and certain other reducing agents retard the reaction, oxygen compounds like the oxide and hydroxide of sodium, and chromium and its compounds accelerate it, and in some cases to a very marked degree. In each of the following series of experiments from 2000 to 2200 grammes of sodium were heated to about 380° in a wrought-iron crucible and ammonia was admitted at the rate of about 90 litres per 5 minutes; the percentages of ammonia decomposed when no catalyst was added and in presence of different quantities of the specified catalysts were determined with the following results.

[1] Eng. P. 1613 (1915).

Catalyst.	Quantity of catalyst added.	Percentage of NH_3 decomposed.
—	—	50·3
Sodium hydroxide	10 gr.	65·7
„ „	40 „	87·7
„ „	60 „	97·2
Chromium sesquioxide	5 „	89·2
Chromium sesquioxide + sodium hydroxide	5 „ + 5 „	97·6
Chromium	5 „	92·8

Sodium Cyanide

Considerable quantities of sodium cyanide are used in the cyanide process of gold extraction, and if only it could be produced at a low enough cost this salt might also be used as a source of ammonia, and of such substances as urea, oxamide, and oxalic acid. For instance, when heated with a solution of sodium hydroxide the cyanide is rapidly and completely transformed into the formate of sodium and ammonia: $NaCN + 2H_2O = H{\cdot}COONa + NH_3$. Hence interest attaches to a catalytic process for the manufacture of sodium cyanide recently patented by Bucher.[1]

So long ago as 1839 Lewis Thompson, when writing on the subject of the wasteful methods of producing cyanides from animal matter then in use, made the following statement: "It occurred to me that the atmosphere might be made to supply, in a very convenient manner, the requisite nitrogen, if allowed to act on a mixture of carbon and potash under favourable circumstances. The experiment proved on trial to be correct, and in some manner exceeded my expectation, for the carbonaceous matter employed may be worked over again many times, and is even improved by each operation. I found it necessary to use iron, for a reason which will be apparent in the explanation of the process; when iron is not employed a much higher temperature is required."

[1] For an interesting account of the development of the process, *see* Bucher, *J. Ind. and Eng. Chem.*, 1917, **9**, 233.

Following up this idea Bucher has studied the synthesis of cyanides from atmospheric nitrogen, and has found that iron is an exceedingly active catalyst in the absorption of nitrogen as alkali cyanide. When a mixture of lamp-black and sodium was heated to a white heat in a current of nitrogen for twenty-five hours, the yield of sodium cyanide obtained was 79 per cent. of the theoretical quantity; other experiments confirmed this, and showed that under such conditions the process of cyanide formation is always slow. On the other hand, when a mixture of finely-powdered iron, lamp-black and sodium was heated in nitrogen it was found that when the temperature reached a low red heat absorption of the nitrogen was practically instantaneous, and 94 per cent. of the sodium was converted into cyanide. The reaction was powerfully exothermic, causing a great elevation of temperature. Other experiments in which alkali carbonates were substituted for the alkali metal led to corresponding results. With mixtures of these salts and carbon at a low red heat there is practically no fixation of nitrogen, but when finely divided iron is added to the mixture the method is an exceedingly efficient one.

These observations formed the basis of a series of patents for the manufacture of alkali cyanides, of which the following [1] may be quoted. In the production of cyanogen compounds from alkali or alkaline earth carbonates, carbon, and nitrogen, the materials are moulded into briquettes, 1 in. long and $\frac{1}{4}$ in. in diameter, which are heated to the required temperature in an electric resistance furnace. Iron is incorporated with the briquettes in order that the reaction may take place at a more moderate temperature, and the briquettes are preheated by the hot waste gases. The charge descends through a narrow vertical furnace where it meets the nitrogen, which has been preheated by using it to cool the final product.

Producer gas may be used instead of nitrogen, the results obtained in similar experiments being practically the same. It is vital, however, that the briquettes should not be allowed

[1] Eng. P. 23292 (1914).

to cool in a current of producer gas, as in that case there is almost complete destruction of the cyanide. Probably this is caused by carbon dioxide produced by the reaction $2CO \rightleftharpoons C + CO_2$, in which iron acts as a catalyst at a low temperature.

A number of modifications of the process, some of which are of a greatly altered character, are protected by later patents.[1]

So far as purely chemical problems are concerned the details of the process appear to have been worked out satisfactorily, but the heating of mixtures of alkali carbonate and carbon to temperatures of from 800° to 900° presents serious mechanical difficulties. It is a very far from simple matter to design plant constructed of materials which will withstand the furnace conditions, and unless this problem is also solved there is no great prospect of successful working of the process.

Hydrazine

Although hydrazine has not as yet found very extensive applications in chemical industry, its uses are of sufficient importance to justify the inclusion of a short account of the very interesting process by which it is obtained.

The best method for the preparation of hydrazine is that discovered by Raschig. His original process [2] consisted in treating a solution of a hypochlorite with excess of ammonia in the cold and then heating the mixture, with the result that the monochloroamine first formed interacted with the excess of ammonia to produce hydrazine. For example, one litre of a solution of sodium hypochlorite containing about 70 grammes of active chlorine is added to one litre of a 20 per cent. solution of ammonia, the temperature being kept below 15°. The mixture is without delay heated to boiling, and by boiling off the excess of ammonia, acidifying with sulphuric acid and evaporating to crystallization the

[1] U.S. P. 1120682, 1138190, 1138191, 1174667, 1174668, 1174944.
[2] Eng. P. 22957 (1907).

hydrazine is isolated as the sparingly soluble sulphate. The yield is about 25 per cent. of the theoretical quantity.

In the first stage of the process monochloroamine is formed by interaction of the hypochlorite and the ammonia :—

$$NH_3 + NaOCl = NH_2Cl + NaOH.$$

The chloroamine in turn may react with the ammonia either (1) with liberation of nitrogen and formation of ammonium chloride : $3NH_2Cl + 2NH_3 = N_2 + 3NH_4Cl$, or (2) with the production of hydrazine hydrochloride :—

$$NH_2Cl + NH_3 = N_2H_4HCl,$$

and the success of the method, so far as the preparation of hydrazine is concerned, depends upon increasing the velocity of the second reaction or retarding that of the first. It has been found [1] that the addition to the mixture of certain liquids thicker than water increases the yields of hydrazine to between 40 and 50 per cent. of the theoretical; such liquids as 5 per cent. solutions of cane sugar, glycerol, dextrin, or starch are suitable for this purpose. Yields of from 60 to 80 per cent. of the theoretical may be obtained by adding solutions of gelatin, albumin, casein, etc., to a mixture of nine parts of a concentrated solution of ammonia and one part of a solution of a hypochlorite containing about 70 grammes of active chlorine per litre.

Production of Nitric Acid by Oxidation of Ammonia

The direct oxidation of ammonia with oxygen, at a sufficiently high temperature, results in the conversion of the ammonia into nitrogen and water :—

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

If, however, the oxidation is carried out in presence of a suitable catalyst the reaction takes such a course that nitric oxide is formed as an intermediate product :—

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

[1] Eng. P. 139 (1908).

In presence of excess of oxygen the nitric oxide is converted into nitric peroxide, which in turn is absorbed by water with formation of nitric acid and, ultimately, nitric oxide. The reactions are essentially as follows :—

(1) $2NO + O_2 \rightleftharpoons 2NO_2$;
(2) $2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$;
(3) $3HNO_2 \rightleftharpoons HNO_3 + H_2O + 2NO$.

The catalytic oxidation of ammonia to nitric acid by means of atmospheric oxygen in presence of platinum was first observed by Kuhlmann in 1830, but the discovery did not receive any practical application until 1902, when it was taken up and developed by Ostwald. Since that date progress has been rapid, and large quantities of nitric acid are now produced from ammonia.

According to Ostwald's original process,[1] a mixture of ammonia and air (the air must be in considerable excess) is passed as rapidly as possible over a heated catalyst composed of platinum. The object of passing the gases over the catalyst with a high velocity is to minimize decomposition of the oxides of nitrogen formed by oxidation of the ammonia. The gases are heated before coming into contact with the catalyst, by means of a heat interchanger, by the hot gases issuing from the contact chamber. If platinum black or spongy platinum is used, there is considerable loss of ammonia due to the formation of free nitrogen, which is to a great extent obviated when compact platinum, or platinum partly covered with the spongy metal, is employed. The catalyst may be variously constructed, for instance, wire netting or perforated plates may be used, or undulated strips of platinum foil, or alternately flat and crumpled slips. Other metals, such as iridium, rhodium or palladium, may replace the platinum.

In the Frank-Caro modification of this process mixtures of ammonia and air are passed through electrically heated platinum nets of 80–100 mesh, and in the Ostwald-Barton process, now installed in several large plants, the principle

[1] Eng. P. 698 (1902); addition to Fr. P. 317544.

is essentially that of the original patent, but the catalyst is distinctly different from that first used by Ostwald. The details of the preparation of the catalyst are kept secret, but it is known to have a very small cross section and to be placed at the end of a 60 mm. tube so arranged that the products of combustion issuing from the tube heat the mixture of air and ammonia as it approaches the catalyst. No external heating is required; the reaction once started continues without interruption, and it is only necessary to force the mixture of gases through the catalyst by means of a blower.

According to a later patent [1] oxidation of atmospheric nitrogen simultaneously with that of ammonia is brought about by passing a mixture of the latter and heated air through a tube containing as catalyst a network of metallic threads (of palladium-platinum, platinum-iridium or other metals of the platinum group), which occupy the whole section of the tube, forming a layer from about 0·1 mm. to 2 mm. in thickness, the transverse section of the tube presenting a free space of at least 100 mm. No electric heating of the metallic net is necessary.

A modification of the process which involves cooling of the gases has also been protected.[2] Ammonia mixed with air in suitable proportions is passed through a catalytic mass maintained at a constant temperature above 500°; a cooling appliance is so arranged as to prevent the gas mixture being heated before it reaches the catalyst. The latter is composed of pure iridium-free platinum wire in the form of gauze or of a grid, heated by a controlled electric current, or else is in the form of powder containing a platinum wire embedded in it, which is heated similarly.

All the processes already mentioned necessitate the use of platinum or other expensive metal of the platinum group, but satisfactory results may be obtained if commoner metals are substituted for platinum and advantage is taken of the well-known influence of activators in promoting the efficiency of the catalyst.

[1] Fr. P. 435397. [2] U.S. P. 1193796–1193800.

Thus it has been proved [1] that the oxidation of ammonia can be effected by passing a mixture of that gas with oxygen or with air over a heated catalyst containing iron or an oxide of iron together with bismuth or an oxide of bismuth as activator; either of these may be replaced by an oxide of a rare earth metal, or a mixture of three or more oxides may be used; the iron may be replaced by a metal of the iron group, for example manganese, chromium or uranium, or indeed by almost any metal or metallic oxide. For instance, 25 parts of ferric nitrate and 1 part of lanthanum nitrate are dissolved in water and precipitated by ammonia. The precipitate is formed into lumps which are dried at 250° and then heated to 600°; this catalyst is used at a temperature of 700°. If a binding material is employed in preparing the catalyst it should not contain any large quantities of non-metallic elements, metalloids, or their compounds. The bismuth or bismuth oxide may be replaced by tellurium, or a tellurium compound, upon a carrier consisting of a noble metal or an indifferent substance, and in an amount which may be varied within wide limits. Thus the following may be used as contact masses at 700°–800°: powdered firebrick soaked in a 10–20 per cent. solution of platinum chloride, and in a solution of about 10 per cent. of sodium or ammonium tellurite; a metal of the platinum group deposited on the carrier and then activated with a small amount of tellurium or one of its compounds; granular cupric oxide soaked in a 5 per cent. solution of ammonium tellurite and then dried. When noble metals, especially those of the platinum group are used in the catalyst, lead may be used as activator instead of a part or the whole of the bismuth or of the tellurium.

Interesting figures illustrating the results obtainable with catalysts consisting of iron containing various promoters have been published by Maxted.[2] Of these the figures for iron with bismuth as promoter, and for iron alone, may be

[1] Eng. P. 13848 (1914), 13297 (1915), 7651 (1915), 13298 (1915).
[2] *J. Soc. Chem. Ind.*, 1917, **36**, 777.

quoted. The experiments were carried out at a temperature of 700°, the ammonia being mixed with a supply of air sufficient for its complete oxidation to nitric acid, but not in excess of that amount.

Catalyst.	Time of contact in seconds.	Yield of nitric acid %.
Iron . . .	0·03	71·0
,, . . .	0·02	82·5
,, . . .	0·015	83·5
,, . . .	0·012	82·5
,, . . .	0·01	75·0
Iron-bismuth . .	0·06	78·0
,, . . .	0·02	90·0
,, . . .	0·015	92·0
,, . . .	0·012	93·4
,, . . .	0·01	94·6
,, . . .	0·0086	91·0

The efficiency of pure iron for the oxidation of ammonia is very appreciably increased by the addition of cerium, thorium, bismuth, tungsten, or copper, the time of contact necessary for the production of the maximum yield of nitric acid varying with the particular promoter used. Thus the most favourable time of contact is, under the conditions of the experiments, about 0·01 second for iron-bismuth, 0·015 second for iron-cerium, and 0·02 second for iron-thorium. In the case of lead, which apparently is not so efficient a promoter as some of the others, the yield of nitric acid is almost independent of the time of contact.

With antimony as promoter a high yield was obtained to begin with, but after some time the results were much the same as with pure iron. The alkali metals, as typified by potassium hydroxides, appear to have little effect on the catalytic activity of iron, whilst calcium was found to reduce very considerably the maximum yield of nitric acid. The same result attended the employment of zinc and manganese as promoters.

It has been claimed [1] that by using thorium oxide, or a mixture of this with other rare earth oxides, as catalyst, ammonia can be oxidized by air at a temperature between 150° and 200°, with a yield of 90 per cent. of nitric or nitrous acids, and also [2] that when burnt pyrites (ferric oxide containing a little cupric oxide) is employed as the contact substance at 600°–750°, nitrous anhydride is the sole product of the oxidation; this when absorbed by solutions of caustic alkalis yields the alkali nitrite.

A yield of from 3 to 4 per cent. by volume of oxides of nitrogen is said [3] to be obtained by burning methane with air enriched with oxygen under high pressure, or by causing the mixture of gases to undergo flameless combustion through contact with a mass of zircon; the consumption of methane is stated to be about 2·5 cub. metres per kilo of 100 per cent. nitric acid. Another method [4] for the fixation of nitrogen in the form of oxides of nitrogen consists in passing a mixture of nitrogen and oxygen, such as air, over an oxidizing catalyst which is heated to a temperature above 500°. The catalysts employed are, in order of decreasing efficiency, the oxides of cobalt, manganese, chromium, nickel, barium, lead, and cerium; finely divided copper may also be used. The gases are preferably cooled immediately after passing over the catalyst by means of a current of cold compressed air blown into the tube through which they escape.

In order to convert the oxides of nitrogen produced by the oxidation of ammonia into nitric acid, it has been proposed [5] to pass a mixture of oxides of nitrogen, oxygen, and ozone, containing less than 74 per cent. of oxygen, over an oxidizing catalyst containing nickel; the nitric anhydride produced by the reaction is absorbed by an aqueous solution of an alkali.

As regards the economic side of the manufacture of nitric acid by oxidizing ammonia with air, Maxted [6] points out

[1] D. R. P. 224329.
[2] *Ibid.* 168272.
[3] *Ibid.* 281084.
[4] Fr. P. 440218.
[5] U.S. P. 1178440.
[6] *Loc. cit.*

that, on account of the high velocity with which the gases are passed over the heated catalyst, a relatively small contact chamber suffices for the oxidation of a comparatively large quantity of ammonia per hour, and, moreover, since practically no power is required for the operation the actual manufacturing costs, exclusive of the cost of materials, should be low. The power required for the production of one ton of nitric acid from ammonia should not exceed 0·015 kilowatt-year, in addition to the cost of condensation and of concentration. As regards the latter items also, the position is a favourable one, for by the oxidation of ammonia gases are obtained of a much higher concentration of nitric oxide than those produced by the arc process. Accordingly much less tower space is required for their absorption, and much stronger solutions of nitric acid can be directly obtained without concentration; a solution containing from 50 to 55 per cent. of nitric acid is easily obtained from the towers as compared with 30–35 per cent. nitric acid in the arc process.

A recent paper [1] states that several large sets of sulphuric acid chambers have for more than a year been producing their normal output of acid without the use of nitre, the necessary oxides of nitrogen being supplied by catalytic oxidation of ammonia.

The catalyst employed is pure platinum in the form of fine gauze four layers thick, the layers being sewn closely together so as to avoid spaces between them. A mixture of ten volumes of air and one volume of ammonia is used. At the start of the process the catalyst is heated up by means of an electrically heated platinum spiral inserted in the apparatus in close contact with the gauze, and the mixture of gases is enriched with ammonia for a moment by turning on a small auxiliary supply. Once the reaction has started, with four layers of gauze and a sufficiently rapid rate of flow of the gases, the heat developed is sufficient to maintain the catalyst at the correct temperature to complete the oxidation without the necessity for any external heating.

[1] Adam, *Chem. Trade Jour.*, 1918, **62**, 181.

Reaction between ammonia and the oxides of nitrogen, resulting in the formation of water and nitrogen or nitrous oxide, takes place readily, hence any slip of ammonia through the gauze will cause a diminished yield through the occurrence of such reactions immediately the gases leave the catalyst. However, with correct thickness of the catalyst layer and with proper adjustment of the rate of passage of the gases through it, complete oxidation of the ammonia is secured. A minimum time of contact of the gases with the catalyst is necessary. If the thickness of the layer of platinum is insufficient and the rate of flow of the mixture of gases slow, the temperature attained is not high enough to keep the catalyst active. With less than four layers of gauze the slip of ammonia is increased, whilst more than four layers give no increased yield; no advantage is gained, but rather the reverse, if the layers of gauze are kept separate.

CHAPTER IV

Hydrogenation

Twenty years ago only a few catalytic methods for the preparation of organic compounds were known and still fewer were in use on the manufacturing scale; to-day, on the contrary, many of these methods are firmly established not only in scientific laboratories but also in industrial establishments, and it is certain that in the future their practical applications will increase in number and in importance.

Amongst such catalytic processes those which involve the use of free hydrogen—processes of hydrogenation—are of special interest, firstly because their discovery gave a decided impetus to research in organic chemistry, and secondly because of their practical value. Previous to the development of these processes hydrogen in the free state was of little use as a reducing agent for carbon compounds; usually other reducing agents were employed, and in cases where hydrogen itself was the most suitable it was applied in the " nascent " state. It has been found, however, that in presence of suitable catalysts hydrogen becomes available as a reducing agent in the case of a very large number of different substances, and moreover that the direct addition of hydrogen to all sorts of unsaturated compounds containing ethylenic or acetylenic linkages and even to the nucleus of aromatic compounds is a process which entails no special difficulties. In this way many substances have been obtained which were hitherto unknown, or of which the preparation by other methods was extremely difficult.

It has been known for a long time that certain metals possess catalytic power, especially when in a finely divided state; for example, early in last century platinum black

was proved by Davy to be capable of causing the union of hydrogen and oxygen. It was not until 1897, however, that any systematic study of the practical application of the catalytic properties of these metals was made. Since that year, in a series of researches continued until the present time, Sabatier in conjunction first with Senderens, and later with other collaborators, has established and extended to a large number of cases a general method for the hydrogenation of volatile organic compounds based upon the use of certain metals in a fine state of division, and particularly of nickel, as catalysts. Of recent years these and many other catalytic methods have been used in many laboratories, and have found extensive applications in research, whilst the value of such methods for manufacturing purposes finds rapidly increasing recognition, as examination of the patent lists will prove. A detailed account of these methods is given in Sabatier's book, *La Catalyse en Chimie Organique* (1913), from which much of the information in the following pages has been derived.

Hydrogenation in Gaseous Systems

Sabatier and Senderens' process consists essentially in passing a mixture of the vapour of the substance to be hydrogenated with excess of hydrogen through a tube containing a metallic catalyst such as platinum black, nickel, cobalt, iron or copper, maintained at a suitable temperature, which is sometimes the ordinary temperature, but generally lies between 150° and 200°; a temperature in the neighbourhood of 180° is frequently the most suitable.

The metals are used in a fine state of division, and, except in the case of platinum, are best prepared by reduction of their oxides with hydrogen in the tube in which the hydrogenation is to take place; this is desirable in order that the activity of the pyrophoric metal should not be impaired by exposure to the air. The catalytic activity of the metals varies greatly according to the method of preparation adopted; an account of some of the best methods is given

in Chapter I. In order to expose an increased surface of the metal to the gases in the tube it is frequently advantageous to distribute it over pumice. This is easily done, for example, by mixing granulated pumice with a thick paste of nickel hydroxide and water, drying in the air bath, and reducing with hydrogen at 220°–300°.

Of the five metals mentioned nickel is the most active, and, indeed, together with cobalt the only one capable of effecting certain hydrogenations such as that of the aromatic nucleus; copper is the least active, whilst platinum and iron occupy an intermediate position between cobalt and copper. Cobalt apparently may be used instead of nickel in all the reactions which the latter is capable of bringing about, but with little advantage, since its activity is less marked than that of nickel and in general higher temperatures are necessary when it is employed. Iron can also replace nickel in many reactions, but not in all. For example, it is possible to use that metal for reducing ethylenic hydrocarbons, acetylene, aldehydes or ketones, but it is useless for transforming the monoxide or the dioxide of carbon into methane and also for the fixation of hydrogen to the aromatic nucleus. Copper is also capable of producing many reductions, though not all, and on account of its cheapness and the ease with which it is obtained from its oxide by reduction at 180°, it may become of commercial importance. It is an excellent metal to use for the reduction of aromatic nitro-compounds to amino-compounds because its action is restricted to the NO_2 group, and does not affect the aromatic nucleus. It may also be used with advantage for the dehydrogenation of different classes of compounds. The behaviour of copper, however, is sometimes entirely different from that of nickel. Platinum black may be used as a catalyst in the hydrogenation of a fairly large number of substances, even at the ordinary temperature. Its activity is superior to that of copper, but it deteriorates rapidly. For example, a mixture of ethylene with hydrogen is transformed into ethane in the cold when passed over platinum black, but after some time the slight deposition of carbon on the metal

prevents the reaction from proceeding at the ordinary temperature and the application of heat becomes necessary. The activity of spongy platinum is much smaller.

The hydrogen to be employed in these reactions must be carefully freed from all traces of impurities such as sulphuretted hydrogen, phosphoretted hydrogen, arseniuretted hydrogen and hydrogen chloride which may be present if the gas is prepared by the action of metals on hydrochloric or sulphuric acids. This may be effected by washing the gas with a fairly concentrated solution of caustic soda, drying with strong sulphuric acid, and then passing it first through a long tube containing copper turnings heated to low redness and finally through another long tube filled with fragments of slightly moistened potassium hydroxide to arrest acid vapours. If electrolytic hydrogen is available it may be used after removing the small quantity of oxygen which it contains by passage through a short tube containing copper turnings at a low red heat and then through a tube containing fragments of potassium hydroxide.

In catalysis with the aid of nickel or other finely divided metals three stages can be observed, an initial period in which the catalyst adapts itself to its function, a period of normal action, and a period of decline. The first is usually of short duration, and doubtless corresponds with the superficial modification which the metal undergoes when first subjected to the action of the vapour of the substance and of the hydrogen. The second period is generally very long and would probably be indefinite if it were possible to prevent entirely the introduction or the formation of substances capable of altering the surface of the metal, such as may easily be derived from the hydrogen or from the substance undergoing hydrogenation or may be produced in the reaction. Traces of sulphur, phosphorus, or arsenic completely suppress the activity of nickel; for example, benzene which has not been freed from all traces of thiophen cannot be transformed into cyclohexane. Moreover, infinitesimal quantities of chlorine, bromine or iodine absolutely poison the metal, the presence of even a minute trace of bromine

in phenol, for instance, preventing the latter being changed into cyclohexanol.

With pure hydrogen and pure substances of sufficient volatility, the same specimen of nickel, if carefully prepared in the first instance, may be used for a long time, even for a month or more. Nevertheless, no matter what care has been expended in removing all catalyst poisons, sooner or later the activity of the catalyst begins to diminish, the more active the metal the more rapid being the change. Traces of toxic matters introduced with the hydrogen or the substance under treatment gradually accumulate, and most frequently small quantities of non-volatile tarry matters are deposited on the surface of the metal, preventing contact with the gases and hindering the reaction. When a specimen of nickel which has become enfeebled is dissolved in dilute hydrochloric acid, there is always a fetid smell of hydrocarbons and a deposit of brown viscous matter. A similar effect is noticed when the reaction gives rise to substances which are only slightly volatile at the temperature of the reaction and which gradually impregnate the metal and diminish its activity. For this reason it is desirable to avoid allowing the metal to become wetted with the liquid under treatment, which may be caused by using an excess of the substance or by a lowering of the temperature of the reaction tube.

Hydrogenation in gaseous systems can only take place within a certain range of temperature. In practice a lower limit is imposed by the fact that both the substance to be transformed and that produced must be maintained in the state of vapour, and whilst up to a certain point increase of temperature accelerates the reaction yet beyond this, which sometimes is not far removed from the point at which the reaction begins, there may be profound changes in its course. Thus the conversion of benzene, C_6H_6, into cyclohexane, C_6H_{12}, by the action of hydrogen in presence of nickel begins at 70°; as the temperature is raised above this point the velocity of the reaction increases, and reaches a maximum at 180°–200°; at still higher temperatures the

amount of cyclohexane formed gradually diminishes, and at 300° the action no longer takes place; on the contrary, at this temperature cyclohexane is decomposed completely into benzene and hydrogen or into benzene and methane, according to the equation: $3C_6H_{12} = 2C_6H_6 + 6CH_4$. When a compound is capable of uniting additively with several molecules of hydrogen it is sometimes possible, by choice of suitable temperatures, to carry out the operation in stages; thus anthracene, $C_{14}H_{10}$, is converted at 180° into the perhydride, $C_{14}H_{24}$, and the decahydride, $C_{14}H_{20}$, at 200° into the octohydride, $C_{14}H_{18}$, and at 260° into the tetrahydride, $C_{14}H_{14}$.

Hydrogenations which can be effected within a wide range of temperature, such as the addition of hydrogen to ethylenic compounds or the reduction of aromatic nitro-compounds are easy to carry out. The most difficult are those in which the maximum and minimum limits of temperature lie close together, as in the hydrogenation of the aromatic nucleus.

The tube containing the catalyst is maintained at the proper temperature in various ways; an air bath, an oil bath, or even a furnace with suitable burners may be used, and a convenient arrangement for electric heating has been described by Brunel.[1] Whatever method be adopted, it is necessary to provide for easy regulation of the temperature and for uniform heating of the tube.

Hydrogenation in Liquid Systems.

Hydrogen in presence of catalysts can be used effectively for the hydrogenation or reduction of organic compounds not only when these substances are in the state of vapour, but also in liquid systems, and many different processes have been devised for applying the principle to liquids. In certain cases these processes are preferable to that of Sabatier.

The method of Ipatiev consists in heating the substance to be hydrogenated in presence of nickel or its oxide, or other metals such as copper, or their oxides, with hydrogen

[1] *Ann. Chim. Phys.*, 1905 (8), **6**, 205.

under a pressure of at least 100 atmospheres. The temperature necessary to bring about the reaction may reach 400°, and the pressure may exceed 100 atmospheres, and of course the necessity for the provision of apparatus capable of withstanding such high pressures and the risk of accident which attends their employment constitute a drawback with respect to the general use of the process.

The results of Ipatiev's work, described in a series of papers appearing principally in the *Journal of the Russian Physical and Chemical Society* from 1906 until the present, are on the whole very similar to those obtained by Sabatier's process. For example, the aromatic nucleus is hydrogenated in all cases, benzene at 250° being completely transformed into cyclohexane in an hour and a half; cyclohexane at 300° is decomposed into benzene, hydrogen, and methane, with deposition of carbon; aliphatic ketones are reduced to secondary alcohols, aromatic ketones to the corresponding hydrocarbons; salts of aromatic acids are largely transformed into their hexahydrides; naphthalene is converted into the tetrahydride and then to the decahydride; quinoline yields chiefly the decahydride; oleic acid at 100° and 60 atmospheres pressure is transformed into stearic acid; camphor yields borneol at 350°.

Other less active metals than nickel can also be employed as catalysts; thus iron at 350°–400° transforms fatty aldehydes into acids, and in presence of copper sodium cinnamate is converted into the phenylpropionate without hydrogenation of the nucleus.

The nature of the metal of which the high-pressure vessel is constructed is found to exert an influence on the hydrogenation of compounds containing ethylenic linkages in presence of oxide of copper. Thus in an iron tube trimethylethylene is readily converted into isopentane, whilst in a copper tube the reaction is incomplete, an equilibrated mixture of trimethylethylene, hydrogen, and isopentane remaining :—

$$C_5H_{10} + H_2 \rightleftharpoons C_5H_{12};$$

in an iron tube, and in absence of oxide of copper, no

hydrogenation occurs. Similar results are obtained with hydroaromatic compounds. Further, hydrogenation in an apparatus made of phosphor bronze, in presence of reduced copper, results in the establishment of an equilibrium, whilst if iron turnings are also present hydrogenation proceeds to the end.[1]

The high pressures employed by Ipatiev are not indispensable for hydrogenation in liquid systems, since the process can in many cases be carried out at the ordinary pressure, and with very satisfactory results, by the employment as catalysts of platinum or palladium or of compounds of these metals such as their chlorides, or even of the commoner catalysing metals, *e. g.* reduced nickel or copper, or of their oxides or other compounds.

Platinum and palladium are used sometimes in the form of colloidal solutions, sometimes as platinum black or palladium black. There is a direct relationship between the catalytic activity of a metal and the extent of its surface, consequently as a general rule the finer the state of division of the metal the more effective it will be. Hence many attempts have been made to utilize metals in the colloidal state as catalysts of hydrogenation, since their activity should then reach a maximum. Colloidal solutions of platinum and of palladium are not difficult to prepare, and it has been found that their stability is considerably increased by the presence of certain organic colloids, such as protalbic and lysalbic acids, proposed by Paal, or gum arabic as suggested by Paal and Skita.[2]

In order to effect hydrogenation with the aid of platinum or of palladium in this form, an aqueous solution of the colloidal metal is added to an alcoholic solution of the substance to be hydrogenated and hydrogen is passed in. The liquid must be kept agitated, and it is frequently of advantage to work under pressures somewhat greater than atmospheric; the course of the reaction is also influenced by changes in temperature. The results obtained are generally very

[1] Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1557.
[2] Cf. Chap. I.

similar to those produced by Sabatier's method, but the aromatic nucleus cannot be hydrogenated by means of colloidal palladium.

Palladium black or platinum black may also be used for hydrogenations, instead of colloidal solutions of these metals. Thus it was proved by Fokin [1] that oleic acid can be converted into stearic acid at the ordinary temperature by the action of hydrogen in presence of either of these catalysts. It is due principally to the work of Willstätter [2] that the process has become of almost general application. The substance to be hydrogenated is dissolved in ether or other suitable solvent, mixed with platinum black, in the proportion of one-third to one-thirtieth of the weight of the substance, and hydrogen led in, the apparatus being shaken continuously. By this method ethylenic linkages are easily saturated; aldehydes and ketones are reduced, even aromatic aldehydes being transformed almost quantitatively into the corresponding alcohols, whilst the other methods of hydrogenation yield hydrocarbons: good results are obtained with aromatic hydrocarbons, which are converted into cyclohexanes, and with the terpenes. As a general rule platinum appears to give more satisfactory results than palladium.

Hydrogenation of unsaturated compounds can also be effected in presence of compounds of the platinum metals without the aid of protective colloids.[3] A small quantity of a solution of palladious choride, or of any other soluble salt of a metal of the platinum group, is added to the unsaturated substance, which may be dissolved or suspended in a liquid if necessary, and the whole is exposed to the action of hydrogen, preferably under increased pressure. The addition of a little of an acid is usually advantageous and dilute hydrochloric acid is recommended, but this is not always necessary, since in many cases the reaction can be carried out by passing

[1] *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 697.

[2] *Ber.*, 1908, **41**, 1475, 2199; 1911, **44**, 3435, 3444; 1912, **45**, 1471; and later papers.

[3] Eng. P. 18996 (1912).

hydrogen through a mixture of the substance to be hydrogenated and a solution of the catalyst.[1] Moreover, it is not always necessary to use the catalyst in solution, since for certain purposes, and particularly for the hydrogenation of oils, a chloride of platinum or of palladium in the solid state mixed with a neutralizing agent such as anhydrous sodium carbonate may be employed.[2] In this case the salts are preferably used in the form of powder.

Another modification of the process is based upon the employment of colloidal solutions of the hydroxides of metals of the platinum group.[3] These are obtained by treating a solution of a salt of the metal with sodium carbonate in presence of gum arabic, and are found to be efficient hydrogen carriers in the hydrogenation of unsaturated compounds, the reaction being possible even in neutral solutions.

Not only platinum and palladium but also the commoner catalysing metals, such as reduced nickel or copper, and oxides or other compounds of these metals may be employed for the direct hydrogenation of liquids, or of substances in solution in water or in organic solvents. This method of treatment is applied on the large scale in the " hardening of fats," and is also available in the case of many other organic compounds.

The reactions produced by means of hydrogen in presence of reduced nickel or of other catalysts may be classified in four groups :—

(1) Reduction without fixation of hydrogen; this class included no reactions of technical importance.
(2) Reduction effected with fixation of hydrogen, as, for instance, the reduction of aromatic nitro-compounds to amines.
(3) Hydrogenation proper, *i. e.* the direct addition of hydrogen to unsaturated compounds, which may be exemplified by the hardening of fats.

[1] Eng. P. 28754 (1912). [2] U.S. P. 1023753.
[3] Eng. P. 16283 (1913).

(4) Hydrogenation effected with decomposition of the molecule of the substance under treatment, which frequently occurs when hydrocarbons are exposed to high temperatures.

Reduction in Gaseous Systems

Production of Methane.

The direct synthesis of methane from its elements can be effected, although with difficulty, by heating pure charcoal in hydrogen at a temperature between 1100° and 1200°.[1] If, however, a mixture of charcoal and finely divided nickel is used instead of charcoal alone, the reaction takes place much more readily and at a far lower temperature. The equilibrium between carbon, hydrogen and methane in presence of metallic nickel, at temperatures between 470° and 620°, has been studied in both directions, that is to say, starting either from methane or from its elements, and from the results obtained it has been calculated that at a pressure of one atmosphere, the proportion of methane present is 98·78 per cent. at 250°, 51·16 per cent. at 536°, and 1·21 per cent. at 850°.[2]

A simple method for the synthesis of methane is afforded by the direct reduction of carbon monoxide by hydrogen in presence of nickel: $CO + 3H_2 = CH_4 + H_2O$. The reaction begins at about 180°–200° and proceeds rapidly without complications at 230°–250°. If the theoretical mixture of one volume of carbon monoxide and three volumes of hydrogen is used the reaction is practically complete and the methane obtained almost pure. The catalyst is not sensibly altered, and will serve to bring about the reduction for an indefinite period. At temperatures above 250° a secondary reaction occurs, namely, the conversion of carbon monoxide into carbon dioxide and carbon: $2CO \rightleftharpoons C + CO_2$, which arises from the special effect exercised by the finely divided nickel on the monoxide under these conditions.

[1] Bone and Coward, *Chem. Soc. Trans.*, 1908, **93**, 1975.

[2] Mayer and Altmayer, *Ber.*, 1907, **40**, 2134.

With the aid of nickel as catalyst carbon dioxide also is easily converted into methane by the action of hydrogen: $CO_2 + 4H_2 = CH_4 + 2H_2O$. In this case the reaction only begins at about 230°. It is rapid at 300°, and up to 400° does not present any appreciable complication. If an excess of hydrogen is employed the carbon dioxide is almost completely converted into methane, hence the reaction affords a method of preparing pure methane.[1] The mixture of gases produced is freed from the last traces of carbon dioxide by treatment with caustic alkalis, dried, and cooled by means of a refrigerator containing liquid air; the methane is then condensed to the liquid state whilst the excess of hydrogen escapes.

The production of methane by such methods can be utilized for the preparation on the industrial scale of a gas rich in methane, with a high calorific power and suitable for heating or for incandescent lighting. Various patents covering this have been taken out, of which the following[2] will serve as an example.

Water gas containing approximately equal volumes of carbon monoxide and of hydrogen is passed over nickel heated to 400°–500°; all the carbon monoxide disappears, being converted partly into methane and partly into carbon dioxide, whilst carbon is deposited on the nickel. The resulting mixture of gases, after removal of the carbon dioxide, may contain 80 per cent. of methane. The mixture of nickel and finely divided carbon which is produced during this stage of the process is then heated at 400°–500° in a current of steam, which tends to produce hydrogen and carbon dioxide, which in turn interact with formation of a certain proportion of methane. The final product is a mixture of hydrogen, methane, and carbon dioxide, and after removal of the last there remains a mixture less rich in methane than that produced in the first stage, but still of high calorific power. The process regenerates the nickel, which can be used over again.

In practice the two stages of the process can be carried on

[1] Fr. P. 356471. [2] *Ibid.* 355900.

simultaneously. Finely divided nickel, heated to a temperature between 400° and 500°, is exposed to the action of a mixture in proper proportions of water gas and superheated steam. A mixture of methane, hydrogen, and carbon dioxide is obtained, from which the last is separated. If the water gas and steam are sufficiently purified, and especially if they are passed over copper turnings heated to about 600° before coming into contact with the nickel, the metal retains its catalytic activity for a practically indefinite time. It is easy to obtain a gas containing 48 per cent. of methane and 52 per cent. of hydrogen, and, unlike coal gas, no appreciable quantity of the highly toxic carbon monoxide. The reaction may be represented by the following equation :—

$$5(CO + H_2) + H_2O = 2CH_4 + 2H_2 + 3CO_2;$$

in practice three volumes of water gas yield one volume of the mixture of hydrogen and methane.

The production of methane from water gas has also been studied by Vignon,[1] who has found that when a mixture of water gas and steam is passed over heated lime methane is produced, whilst the proportion of carbon monoxide in the gas is, of course, reduced and that of hydrogen increased. At temperatures below 850° calcium carbonate is formed, but at higher temperatures the calcium carbonate is decomposed, and the resulting mixture of gases contains carbon dioxide also. Small quantities of other hydrocarbons such as ethylene are likewise formed. Iron filings, copper turnings, silica, magnesia, or alumina may be used in place of lime. Above 900° lime acts as a catalyst in the following reactions, to which Vignon attributes the presence of methane in water gas :—

(1) $4CO + 2H_2O = 3CO_2 + CH_4$;
(2) $2CO + 2H_2 = CH_4 + CO_2$;
(3) $CO_2 + 4H_2 = CH_4 + 2H_2O$.

Further experiments in this direction showed that the reaction between steam and heated carbon, which results

[1] Fr. P. 416699, 469907.

in the formation of water gas ($C + H_2O = CO + H_2$), takes place more rapidly and at a lower temperature if a mixture of carbon and lime is used instead of carbon alone, and that the gas produced contains methane as well as hydrogen and carbon monoxide. Hence the original process was modified as follows: Steam is passed continuously through a chamber packed with an intimate mixture of about 100 parts of coke and 250 parts of quicklime, heated from without to a temperature between 600° and 800°; the formation of water gas and the conversion of the carbon monoxide in the water gas into methane are thus realized in a single apparatus worked continuously.

Vignon has attempted to devise a scheme for the complete gasification of the carbon of coal so as to produce a combustible gas containing a low percentage of carbon monoxide. In this process [1] lime is added to coal, and the whole distilled at a temperature between 900° and 950°, whereby a yield of about 12,000 cub. ft. of gas per ton of coal is obtained. Steam is then passed over the residual mixture of coke and lime, heated to 900°–1000°, which increases the yield of gas to about 72,000 cub. ft. per ton of coal treated. The mixed gas has the approximate composition, hydrogen 70–78 per cent., methane 15–20 per cent., carbon monoxide 5–10 per cent. The calorific value is only slightly inferior to that of coal gas, the volume obtained is from eight to ten times greater than that yielded by simple distillation of the coal, and practically all the nitrogen of the coal is converted into ammonia.

Reduction of Aromatic Nitro-compounds.

For some years past strenuous efforts have been made to ascertain the most favourable working conditions for reducing aromatic nitro-compounds with hydrogen or with gaseous mixtures containing hydrogen in the presence of catalysts. These reactions are carried out at temperatures sufficiently high to maintain the nitro-compounds in the state of vapour,

[1] Cf. Fr. P. 477083.

sometimes under increased pressure in the presence of water vapour and sometimes at the ordinary pressure and in absence of water.

Sabatier found reduced copper to be a better catalyst than other metals for the reduction of nitro-compounds by means of hydrogen, because its action is very regular and does not extend to the aromatic nucleus. Nitrobenzene is thus transformed into aniline at temperatures above 230°: $C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O$. The reaction is rapid between 300° and 400°, and provided that excess of hydrogen is present the aniline produced contains only traces of nitrobenzene and of azobenzene. The yield is 98 per cent. of the theoretical, and the same catalyst can be used for a long time. The hydrogen may be replaced by water gas, since the carbon monoxide present in the latter plays a useful part, being partly oxidized to carbon dioxide.[1]

The toluidines can be prepared equally well from the nitrotoluenes under similar conditions, and α-nitronaphthalene is easily converted into α-naphthylamine at 330°–350° and the chloronitrobenzenes into chloroaminobenzenes at 360°–380°.

Other proposed methods for the preparation of aromatic amino-compounds include the following:—

Nitro-compounds are reduced by hydrogen or by mixtures of hydrogen with other gases, such as carbon dioxide or gases containing carbon dioxide, in presence of water and a catalyst under high pressure and at a temperature above the boiling point of the amine produced. Iron is used as catalyst.[2]

Nitro-compounds volatile in steam are carried in the state of vapour by this medium, together with hydrogen, over catalysts heated to temperatures considerably below the boiling points of the compounds. For example, nitrobenzene is heated to 120° and a mixture of steam and hydrogen is passed through the liquid. The resulting gaseous mixture is passed through a long tube half filled with finely divided

[1] Fr. P. 312615. [2] D. R. P. 282492.

nickel and heated to 120°, and the issuing vapours are condensed. The yield of aniline is almost theoretical.[1]

The use of a catalyst in the form of copper together with an activator for the reduction of nitro-compounds by hydrogen has also been protected. The copper is prepared by ignition of a salt of the metal or by reduction of a salt with hydrogen or with carbon monoxide at temperatures below a red heat; suitable salts are such as give indifferent gases on heating, *e.g.* the formate, oxalate, or nitrate, or mixtures of copper salts with ammonium carbonate. The copper may be used us such, or distributed on pumice, asbestos, or kieselguhr, with the addition of activators such as alkali compounds or metallic oxides such as magnesia or alumina. The reduction of the nitro-compound should be carried out at or below 200°; at higher temperatures impure products are obtained and the activity of the catalyst may decrease.[2]

A later patent[3] prescribes different methods for the preparation of a suitable catalyst. For example, a hot solution of caustic soda is added gradually to a solution containing 1180 gr. of copper nitrate crystals, 38 gr. of silver nitrate and 252 gr. of magnesium nitrate crystals, and the precipitate is washed and mixed with 130 gr. of pumice stone in lumps and a small quantity of water; 20 gr. of a 40 per cent. solution of sodium silicate are then added, and the pasty mass obtained is heated at 200° in a current of hydrogen. Aniline is obtained when a mixture of hydrogen and the vapour of nitrobenzene is passed over this catalyst at a temperature of 200°–210°.

Pumice coated with silver or with gold is said to be an effective catalyst for the reduction of nitrobenzene by hydrogen at temperatures of 230° and 230°–250° respectively,[4] as also are ferrous oxide, or the magnetic oxide of iron, mixed with asbestos or kieselguhr; the oxides are not reduced during the process.[5]

The use of carbon monoxide, or gases containing carbon

[1] D. R. P. 282492.
[2] *Ibid.* 282568.
[3] Eng. P. 5692 (1915).
[4] D. R. P. 263396.
[5] Fr. P. 462006.

monoxide, together with water vapour at comparatively low temperatures for the manufacture of aniline, other aromatic amines, or other compounds by catalytic hydrogenation has also been protected.[1] As an example, the vapour of nitrobenzene mixed with an excess of a reducing gas containing at least one volume of water vapour for each three volumes of carbon monoxide is passed over a contact mass containing copper. The temperature is maintained at 200°–220° during the reduction, and a good yield of aniline is obtained. The catalyst may be prepared by coating 130 gr. of pumice with a mixture of 24·3 gr. of copper carbonate, 2·7 gr. of zinc carbonate, and 20 gr. of commercial sodium silicate solution, and reducing at a low temperature.

p-Aminophenol can be prepared from *p*-nitrophenol by catalytic reduction in presence of nickel,[2] and it is also stated that with copper as the catalyst aliphatic nitro-compounds are reduced by hydrogen at temperatures between 180° and 200°, giving good yields of the corresponding amines.

Reduction of Aldehydes and of Ketones.

Results which may prove to be of technical importance have been obtained by subjecting aldehydes and ketones to the action of hydrogen in presence of nickel at high temperatures, when, especially in the case of the latter compounds, the >CO radicle is reduced to the >CHOH radicle.

In this manner aliphatic aldehydes can be transformed into primary alcohols at temperatures below 180°, as a rule without the formation of secondary products; aromatic aldehydes, on the other hand, tend to yield hydrocarbons. Benzaldehyde, for example, when hydrogenated at a temperature between 210° and 235°, gives a mixture of benzene and toluene, with a certain proportion of their hexahydrides.

Aliphatic ketones being more stable than aldehydes when in contact with nickel can be reduced with the formation

[1] Eng. P. 6409 (1915). [2] *Ibid.* 16936 (1912).

of secondary alcohols. No other products such as pinacones are formed, as is the case when ketones are reduced by means of sodium amalgam and water, and since the yield is usually almost quantitative, the method is a very advantageous one. Thus isopropyl alcohol can be prepared very economically by passing a mixture of the vapour of acetone and hydrogen over nickel heated to a temperature of 115°–125°: $CH_3 \cdot CO \cdot CH_3 + H_2 = CH_3 \cdot CHOH \cdot CH_3$. Equally good results are obtained with higher ketones; at temperatures above 200°, however, the reaction takes a different course, and, instead of alcohols, mixtures of higher ketones are produced. Cyclohexanone is readily converted into cyclohexanol, with production of only a small quantity of cyclohexane, by hydrogenation below 180°. Mixed ketones such as acetophenone do not give alcohols, but the corresponding hydrocarbon—in the case quoted, ethylbenzene—and if the nickel is active hydrogenation of the aromatic nucleus also occurs.

Reduction in Liquid Systems

Preparation of Indigo White from Indigotin.

The methods of reduction illustrated in the preceding pages are all carried out at high temperatures, but it is not in all cases necessary that the substance to be reduced should be in the state of vapour when exposed to the action of hydrogen in presence of a catalyst. For instance, aldehydes and ketones can be reduced under high pressure, by Ipatiev's method, with results very similar to those obtained when the compounds are in the state of vapour, and also by subjecting them to the action of hydrogen at the ordinary pressure in presence of platinum or palladium in colloidal solution or of platinum black. The last-named catalyst is particularly valuable, since with its aid the aromatic aldehydes, which yield hydrocarbons when hydrogenated by the methods already described, are easily and completely reduced to the corresponding aromatic alcohols.[1]

[1] Vavon, *Compt. rend.*, 1912, **154**, 359.

Moreover, it has been found that the hydrogenation or reduction of liquids may frequently be effected through the catalytic action of common metals, especially nickel, without recourse to high temperatures or pressures. The proportion of active nickel employed may be as low as from 0·1 to 0·05 per cent. of the weight of the liquid in some cases, and the method is applicable to various classes of compounds. Thus by this method it is possible to reduce benzaldehyde to benzyl alcohol, acetophenone to phenylmethyl carbinol, *p*-nitrophenol to *p*-aminophenol, and *p*-nitroaniline to *p*-phenylenediamine; or, again, to hydrogenate compounds containing ethylenic linkages, such as cinnamic acid and isoeugenol.

The process, in its original form,[1] is carried out by passing hydrogen, or a gaseous mixture containing hydrogen, into the substance to be treated, which is either in the liquid form or in solution or suspension in a suitable liquid, in presence of the active metal. The mixture is agitated vigorously, and the velocity of the reaction is increased by working under pressure, although extremely high pressures are not necessary. For example, phenol containing 1 per cent. of reduced nickel, and heated to 100°–120°, is treated with hydrogen under a pressure of 10–15 kilos per sq. cm. If the mixture is thoroughly agitated the whole of the phenol is converted into cyclohexanol :—

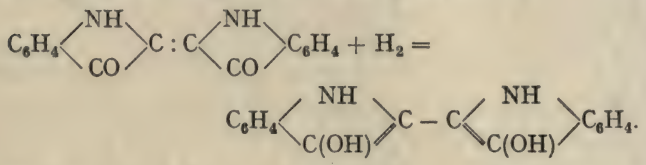
$$C_6H_5{\cdot}OH + 3H_2 = C_6H_{11}{\cdot}OH.$$

The process can be modified by addition of catalysts of the second order, or of acids or alkalis, etc., so as to alter the speed of the reaction or to produce different results. Thus the reduction of nitrobenzene by the aid of reduced nickel leads to the formation of aniline alone when the original method is employed, but when sodium hydroxide is also added azoxybenzene is the principal product; this in turn is reduced to azobenzene, which can be further reduced to hydrazobenzene, in each case if alkali is present; in neutral media azoxybenzene is converted into aniline. Vigorous

[1] Brochet, *Compt. rend.*, 1914, **158**, 1351; **159**, 190, 326.

shaking is preferably substituted for the high pressure first recommended.

An important application of the process is the reduction of indigotin or indigo blue to indigo white : [1]



Indigotin suspended in a dilute solution of sodium hydroxide is rapidly reduced by hydrogen at a temperature between 60° and 80° in the presence of active nickel, the emulsion being well agitated. The catalyst can be separated by filtration, and the solution of indigo white thus prepared is free from any excess of the reducing agent, which is present, for instance, when the reduction is effected by an alkali hydrosulphite. The activity of the nickel for this reduction is retained even after immersion in water for one year. The reaction may be accelerated by heating under pressure.

The process is applicable to the production of leuco-derivatives of other vat dyes, and yields these substances free from the reducing agents employed in the older vats; nothing but an alkali salt or the like, added to promote the reduction, remains. In the case of indigo the caustic alkali may be replaced by lime, or even a neutral vat may be employed; in the latter case, however, the reaction is much slower. The process may be so adapted as to produce indigo white in the form of a concentrated solution or a paste.

These results are very suggestive, inasmuch as a diminution in the alkalinity of the vat would increase the value and widen the range of application of vat dyes.

In this connection it may be noted that according to an older patent [2] the reduction of indigo to its leuco-derivative is facilitated by adding a small quantity of Induline Scarlet

[1] Fr. P. 473536; Eng. P. 19848 (1914). [2] D. R. P. 29918.

either to the alkaline vat or to the dye itself. Indigo is also rendered more easily reducible by the addition of benzyl sulphanilic acid to the vat.[1]

Preparation of Formic Acid from Carbonic Acid.

Free formic acid is obtained directly by reducing carbon dioxide with hydrogen under high pressure in presence of water and a catalyst :—

$$HO{\cdot}CO{\cdot}OH + H_2 = H{\cdot}COOH + H_2O.$$

Thus, when 150 gr. of water containing 3 gr. of palladium black in suspension are vigorously agitated by the injection of a gaseous mixture containing 64 per cent. of hydrogen and 36 per cent. of carbon dioxide under a pressure of 110 atmospheres, the temperature being maintained at 20°, a 1 per cent. solution of formic acid is obtained. Under higher pressures the yield is considerably greater.[2]

Formates also are obtainable on a commercial scale by the action of compressed hydrogen on aqueous solutions of bicarbonates in presence of catalysts :—

$$e.g.\ HO{\cdot}COONa + H_2 = H{\cdot}COONa + H_2O.$$

A 75 per cent. yield of potassium formate is obtained by passing hydrogen under a pressure of 60 atmospheres vigorously through 200 c.c. of a 5 per cent. solution of potassium carbonate containing 1·5 gr. of palladium black at a temperature of 70°; a 70 per cent. yield of sodium formate is obtained in eight hours by passing simultaneously hydrogen and carbon dioxide at 30 atmospheres pressure through a solution of borax of similar concentration in presence of the same catalyst; calcium formate is prepared from the carbonate by mixing it with water and palladium black, and then passing in carbon dioxide at 20 atmospheres and hydrogen at 50 atmospheres pressure for several hours.[3]

[1] Eng. P. 18761 (1910). [2] *Ibid.* 9762 (1915).
[3] *Ibid.* 801 (1915).

Electrolytic Reductions.

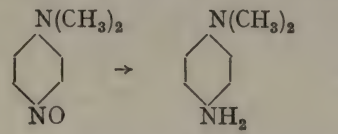
In the reduction of carbon compounds by electrolytic processes it is often observed that the material of which the cathode is composed has an influence on the velocity of the reactions; not infrequently this may be attributed to a catalytic action. For example, aromatic nitro-compounds in alkaline suspension are reduced to amines most advantageously when a copper cathode is employed, whilst, on the other hand, the reduction of pyridine to piperidine proceeds considerably more rapidly when the cathode is of lead. In many other cases there is no doubt that the reduction process is facilitated by the addition of suitable catalysts to the cathodic electrolyte.

The electrolytic reduction of aromatic nitro-compounds in solution in sulphuric or hydrochloric acid usually leads to the formation of aminophenols, but, under definite conditions, also gives amines as the sole products if an indifferent cathode made of platinum, lead, or carbon is used, and if at the same time a small quantity of another metal or of a metallic salt, especially tin or copper, or a salt of these metals, is added to the cathodic electrolyte. For example, aniline is obtained from nitrobenzene under the following conditions: the anode compartment contains 30 per cent. sulphuric acid; the cathodic liquid is a cooled mixture of 12 parts of nitrobenzene, 75 volumes of fuming hydrochloric acid, 50 volumes of water, and 2 parts of stannous chloride. The cathode is made of nickel gauze; current 1000 amp. per sq. metre at 8·5 volts. When the first lot of nitrobenzene is reduced more is added and the process continued. If a platinum cathode is used the addition of metallic copper or of a salt of copper or of iron to the cathode electrolyte is recommended.[1]

Titanium salts may also be used as catalysts in the reduction of nitro- or of nitroso-compounds, and in this case no diaphragm is necessary. Thus the preparation of *p*-di-

[1] D. R. P. 116942 and 117007.

methylphenylene diamine is effected by the electrolytic reduction of *p*-nitrosodimethylaniline dissolved in 11 per cent. sulphuric acid which contains 2 per cent. of titanous sulphate; a nickel cathode is used.[1]

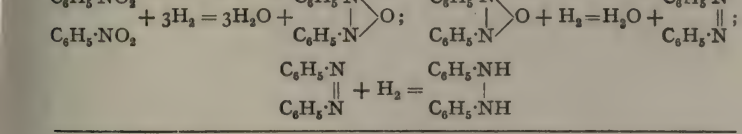


The production of benzidine from azobenzene is easily effected by an electrolytic method when titanium salts are used as catalysts. The azobenzene is suspended in 30 per cent. sulphuric acid containing 10 per cent. of titanous sulphate; a lead cathode is used with a current of 3–4 amp. per sq. dcm. at 3–4 volts. Instead of the titanous salt, vanadium trioxide,[2] in the proportion of 2 parts of the oxide to 100 parts of sulphuric acid, is an effective catalyst :—

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + H_2 = C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5 = NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2.$$

In a similar manner azoxybenzene may be reduced to hydrazobenzene.[3]

The electrolytic reduction of aromatic nitro-compounds to azo- or hydrazo-compounds takes place smoothly if an alkaline solution of a plumbite is used with a lead cathode, even if the nitro-compound is only suspended in the liquid. In presence of finely divided lead or of compounds of lead the reduction of nitro-compounds to hydrazo-compounds also takes place readily :—[4]



[1] D. R. P. 168273.

[2] In oxidation processes the higher oxides of vanadium act as catalysts, in processes of reduction on the other hand the lower oxides.

[3] D. R. P. 168273 and 172654.

[4] *Ibid.* 81129, 121899, and 141535.

Reduction with Sulphurous Acid.

The reducing action of sulphurous acid is in many cases promoted by the presence of hydriodic acid. For example, in preparing benzidine from azobenzene very small quantities of hydriodic acid serve to bring about the reduction of large quantities of the azobenzene through the action of sulphurous acid.

Forty-five parts of finely ground azobenzene are suspended in 250 parts by volume of aqueous hydrochloric acid of sp. gr. 1·18 and 5 parts of potassium iodide are added. Sulphur dioxide is passed through the mixture, care being taken that the benzidine sulphate which separates does not carry down with it unattacked azobenzene. At the beginning of the reaction the sulphur dioxide is very quickly absorbed. When the reaction is complete, the benzidine sulphate is removed and the liquid used again.

Homologues and derivatives of azobenzene, such as azotoluene, azoanisole, and azobenzene-sulphonic acid, can also be reduced by this method.[1]

Reduction with Iron and an Acid.

It is well known that in the reduction of aromatic nitrocompounds to amines by the action of iron and an acid, the quantity of the acid which is necessary is much less than that theoretically required. If iron and hydrochloric acid are employed the reduction of nitrobenzene is effected on the manufacturing scale with not more than $\frac{1}{10}$ of the quantity of acid calculated from the equation—

$$C_6H_5{\cdot}NO_2 + 3Fe + 6HCl = C_6H_5{\cdot}NH_2 + 3FeCl_2 + 2H_2O.$$

This fact finds an explanation in the catalytic activity of the ferrous salt which is produced.

There is difference of opinion as to the course of the reaction, but many chemists hold that the ferrous salt in solution is converted into a basic salt at the expense of

[1] D. R. P. 172569.

the oxygen of the nitro-compound, which undergoes reduction, and that the basic salt in turn reacts with the iron in such a way that ferrous chloride is regenerated:—

$$24FeCl_2 + 4C_6H_5{\cdot}NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_6H_5{\cdot}NH_2.$$
$$12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2.$$

Another explanation of the reaction is that the ferrous chloride produced acts as a carrier, and the reduction proceeds through the action of iron and water:—

$$C_6H_5{\cdot}NO_2 + 2Fe + 6HCl = C_6H_5{\cdot}NH_2 + 2FeCl_3 + 2H_2O.$$
$$C_6H_5{\cdot}NO_2 + 2Fe + 4H_2O = C_6H_5{\cdot}NH_2 + 2Fe(OH)_3.$$

The velocity of the reaction depends upon the quantity of ferrous chloride present, and also varies with the amount of acid in the solution.

Reduction with Hydrosulphites and Formaldehyde Sulphoxylates.

In discharging a number of dyes employed in pattern printing on textile fabrics, the addition of a catalyst to the reducing agent has been found to increase its efficiency in a very marked manner.[1] Naphthylamine Bordeaux, Paranitraniline Red, Chloranisidine Orange, *o*-Nitrotoluidine Yellow, Dianisidine Black, Chrysoidine Bistre and analogous compounds are discharged by means of neutral or slightly alkaline pastes containing sodium formaldehyde sulphoxylate along with a metal, metallic oxide, or metallic salt, which either itself is a reducing agent or is capable of acting as a carrier of the reducing power of the sulphoxylate; the salts of iron, *e. g.* ferrous sulphate or ferric chloride, are preferred as catalysts.[2]

Somewhat later the remarkable discovery was made that the effect of the colour discharging agent is much intensified by the addition to it of small quantities of certain dyes

[1] Baumann, Thesmar, and Hug, *J. Soc. Chem. Ind.*, 1906, **25**, 371, 689.

[2] Eng. P. 15524.

themselves. For example, sodium hydrosulphite (hyposulphite) employed in a neutral medium, *e. g.* in the presence of dextrin and glycerol, gives an imperfect discharge on tissues dyed with α-Naphthylamine Claret, but complete discharge takes place readily when certain basic dyes, for instance, Thionine Blue, Auramine, or Rhodamine 6G., are added to the mixture. With sodium formaldehyde sulphoxylate also some dyes appear to have a catalytic effect in promoting the discharge of colours; those which have been found to act most powerfully in this direction are Setopaline and Nitroalizarine; Rhodamine G. and Acridine Yellow act in a similar manner, but their effect is not so marked.[1]

Addition of Hydrogen to Unsaturated Compounds in Gaseous Systems

Hydrogenation of Olefines and their Derivatives.

Sabatier and Senderens discovered that when nickel is used as the catalyst compounds containing the ethylenic linkage are very readily attacked by hydrogen and converted into saturated compounds.

Ethylene itself, in presence of finely divided nickel, begins to unite with hydrogen at temperatures above 30°; the reaction, which proceeds with evolution of heat, yields ethane as sole product: $CH_2{:}CH_2 + H_2 = CH_3{\cdot}CH_3$. The hydrogen is rapidly absorbed at 130°–150°; if an excess is used all the ethylene is hydrogenated, but if an excess of ethylene is present the product is a mixture of ethane and ethylene from which the latter can be readily separated, *e. g.* by the action of bromine, leaving pure ethane. At 300° and upwards the nickel has a destructive effect on the ethylene, which is decomposed with deposition of carbon and production of a mixture of methane with varying quantities of hydrogen together with a certain proportion of higher hydrocarbons condensible to the liquid state.

The higher olefines are similarly transformed into paraffins if the temperature does not exceed 160°, but above

[1] Wilhelm, *J. Soc. Chem. Ind.*, 1906, **25**, 690.

this point, and particularly towards 300°, there may be partial fission of the carbon chain with formation of paraffins containing a smaller number of carbon atoms and of a small proportion of more complex hydrocarbons.

Alcohols, aldehydes, ketones, acids, etc., of the olefine series can also be converted by this process into saturated compounds. Thus if the vapours of oleic acid are carried by a vigorous current of hydrogen over nickel heated to a temperature of 280°–300°, the oleic acid is rapidly transformed into stearic acid.

These experiments have found at least one technical application in the preparation from ethylene of ethane, which was required for use in a refrigerating machine.[1]

Purified ethylene mixed with hydrogen in equal volume was passed through tubes containing finely divided and freshly reduced nickel. The tubes, four in number, were one metre in length; the first two tubes were coupled parallel with each other, and the gas issuing from each of these was mixed and passed through the other tubes coupled in series. The diameter of the tubes was fixed by experiment, so that with a certain velocity of the current of gas the heat produced by the combination of the ethylene with the hydrogen was insufficient to raise the temperature to the point at which ethane begins to decompose. With a current of 2 cub. metres per hour a suitable diameter was 7·5 cm.; with the same velocity of current and increased diameter of the tubes, cooling was found to be necessary. The requisite temperature, 200°, can be maintained with very little external heating. At atmospheric pressure the formation of ethane was not quantitative, the best samples of the gas containing about 80 per cent. of ethane, 10 per cent. of ethylene and 10 per cent. of hydrogen. Since the formation of ethane by the union of ethylene with hydrogen is attended by a diminution in the number of molecules, it must necessarily prove advantageous to bring about the combination of the gases under increased pressure, but it was found that when equal volumes of ethylene and of

[1] Sprent, *J. Soc. Chem. Ind.*, 1913, **32**, 171.

hydrogen were used under these conditions, the sudden rise of temperature resulting from the combination of so much of the gases in a limited space made the control of the operation uncertain and precarious. Complete success, however, attended the use of the mixture of gases containing about 80 per cent. of ethane alluded to above. This mixture was collected in a gasometer and by means of a gas compressor passed through an iron autoclave filled with fragments of pumice stone saturated with nickel, at a pressure of from 30 to 40 atmospheres. The issuing gas, pure ethane, was liquefied in a steel cylinder. It proved advisable to work with a slight excess of hydrogen, which can be removed by opening the valve of the cylinder containing the liquid ethane. With the small plant described, 25 kilos of ethane could be made daily.

Before bringing the ethylene into contact with the catalyst it must be carefully purified. With this object it is recommended [1] that the gas should be freed from known contact poisons, and then thoroughly washed with concentrated sulphuric acid in order to remove other poisons of undetermined composition. It is advisable after this treatment to pass the purified gas over solid sodium hydroxide in order to remove traces of sulphur dioxide.

Hydrogenation of Acetylene.

When a mixture of hydrogen with a small proportion of acetylene is passed over reduced nickel at the ordinary temperature, the metal becomes warm, the elevation of temperature corresponding with the proportion of acetylene in the gas. With a mixture of two volumes of hydrogen and one volume of acetylene the temperature of the foremost portion of the column of nickel may reach 150°. At the same time the contraction of the gas is greater than that which would follow from the formation of ethane ($\underset{1\text{ vol.}}{CH{:}CH} + \underset{2\text{ vols.}}{2H_2} = \underset{1\text{ vol.}}{CH_3{\cdot}CH_3}$), the volume being reduced to one-fourth of the original, although a little unchanged

[1] D. R. P. 265297.

acetylene and some ethylene due to incomplete hydrogenation remain. This arises from the fact that a considerable proportion of higher paraffins, of which a part may be condensed to the liquid state, is also produced.

In presence of excess of hydrogen ethane is almost the sole product of the reaction, but if the proportion of acetylene is increased the metal becomes hotter, the liquid products are formed in increasing quantity, and the presence among them of aromatic and hydroaromatic hydrocarbons can be proved.

It is claimed [1] that ethylene may be prepared by the action of hydrogen on acetylene—

$$CH{:}CH + H_2 = CH_2{:}CH_2$$

in presence of a catalyst composed of at least one metal of the platinum or of the palladium family, together with one of the following metals: iron, nickel, cobalt, silver, magnesium, zinc, cadmium, and aluminium. The catalyst is used in such a form that an adequate free surface of each of the metals is exposed to the mixed gases. The commoner metals act as protective agents for the rarer metals since they combine more readily with any impurities present in the gases.

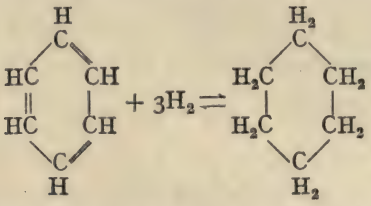
Hydrogenation of Aromatic Compounds.

The preparation and investigation of the hydrogenated aromatic (hydroaromatic) compounds is of very great importance, if only on account of their close connection with the "naphthenes" found in petroleum and with the naturally occurring terpenes and camphors. Until recently the direct hydrogenation of the aromatic nucleus has always been considered extremely difficult to carry out; it is true that many hydroaromatic compounds have been obtained by indirect methods, but their direct formation from aromatic compounds, which is now possible through the application of Sabatier and Senderens' reaction, is of the greatest service to chemists. In the great majority of cases the

[1] D. R. P. 253160.

hydrogenation of the aromatic nucleus by hydrogen in presence of reduced nickel takes place at a temperature of about 180°, most frequently without the occurrence of any secondary reactions, and consequently the products are obtained in very good yields.

When a mixture of the vapour of benzene and hydrogen is passed over finely divided nickel at 170°–190°, the benzene is rapidly transformed into cyclohexane. The condensed cyclohexane usually contains a small proportion of benzene



which has escaped hydrogenation, but this is easily removed by shaking the liquid with a mixture of 1 volume of fuming nitric acid and 2 volumes of concentrated sulphuric acid, which does not attack the cyclohexane.

The hydrogenation of benzene begins at 70° and proceeds with increasing velocity as the temperature is raised up to about 200°; above 200° and especially towards 300° there is practically no formation of cyclohexane, but on the other hand some of the benzene is decomposed into methane and a little carbon is deposited on the metal.

The homologues of benzene behave in a similar way. Below 250° toluene, the xylenes, mesitylene and other homologues containing none but methyl groups give in almost quantitative yields the corresponding methyl derivatives of cyclohexane. In the case of aromatic hydrocarbons with longer side chains there is always produced, in addition to the normal product, a larger or smaller proportion of saturated hydrocarbons with shorter side chains; for example, ethylbenzene yields ethylcyclohexane and some methylcyclohexane, and propylbenzene gives propylcyclohexane together with some methyl and ethylcyclohexanes. The amounts of these secondary products increase with

rise of temperature, and it is, therefore, important to carry out these hydrogenations in the neighbourhood of 180°. If the temperature is raised to 300° the formation of these cyclohexane derivatives diminishes and then ceases, because, as in the case of benzene itself, the reverse action of dehydrogenation sets in and becomes more rapid as the temperature rises.

Not only the aromatic hydrocarbons but also a number of their derivatives can likewise be converted into hydroaromatic compounds. Phenol at 180° is easily hydrogenated, yielding cyclohexanol, $C_6H_{11}\cdot OH$, containing only small quantities of unaltered phenol and of cyclohexanone and cyclohexane; thymol and carvacrol give good yields of the corresponding methylisopropylhexanols at 180°–185° and 195°–200° respectively; esters of the aromatic acids, but not the free acids themselves, are readily converted into esters of the corresponding acids derived from cyclohexane.

Finally, the more complex hydrocarbons such as naphthalene, anthracene, and phenanthrene, and also heterocyclic compounds, for example, pyrrole, pyridine, quinoline and carbazole, all undergo hydrogenation at suitable temperatures under the catalytic influence of nickel. The applications of the reaction are indeed very numerous and very varied.

Hydrogenation in Liquid Systems

As has been pointed out already the combination of unsaturated compounds with hydrogen can be brought about with the aid of catalysts not only when the compounds are in the state of vapour, but also when they are in liquid form or in solution in suitable solvents, either at the atmospheric pressure or under increased pressure. Undoubtedly many applications of this method of hydrogenation will prove to be of technical value, but hitherto the attention of chemists has been largely given to two of these, namely, the hydrogenation of oils and liquid fats and the hydrogenation of alkaloids.

Hydrogenation of Alkaloids.

During the last few years many patents, of which the following will serve as examples, have been taken out which

cover the reduction of alkaloids by means of free hydrogen with the aid of a catalyst. It is quite probable that the medical properties of the products thus obtained will render some of them at least of importance as drugs. Certainly the properties of these products differ considerably from those of the original alkaloids; thus, for example, the physiological effects of dihydromorphine are more lasting than those of morphine itself.

Strychnine dissolved in dilute acetic acid containing a little of a 1 per cent. solution of palladious chloride and of a solution of gum arabic of similar strength is reduced by hydrogen under two atmospheres pressure to the dihydride, and under three atmospheres to the tetrahydride. Brucine under similar conditions yields the dihydride.[1]

Hydrides of the cinchona alkaloids are prepared by treating the alkaloids with hydrogen in presence of a colloidal metal of the platinum group.[2] The colloidal solutions of these metals may be replaced by the metals themselves, which are best used when in a finely divided condition or deposited on an inert substance. For instance, 1 part of platinum black is added to a solution of 250 parts of quinine sulphate in 1400 parts of water and 40 parts of sulphuric acid, and the mixture is shaken with hydrogen under a slightly increased pressure until it is stable towards permanganate. After filtration the solution is neutralized when hot, when hydroquinine sulphate will at once separate in fine needles.[3]

Under similar conditions morphine and codeine yield dihydro-derivatives,[4] whilst dihydrocodeine may be also prepared by the methylation of dihydromorphine. The latter compound can be obtained not only from morphine but also from the mixture produced by hydrogenating opium.[5]

Colchicine treated with hydrogen in presence of finely divided platinum or of a colloidal solution of the metal yields a reduction product, probably the tetrahydro-derivative, which is less toxic than colchicine itself.[6]

[1] D. R. P. 230724.
[2] U.S. P. 989664.
[3] Eng. P. 3948 (1912).
[4] D. R. P. 260233.
[5] *Ibid.* 278107.
[6] *Ibid.* 279999.

In presence of colloidal platinum, pyridine and its homologues when dissolved in acetic acid are reduced to hexahydropyridine, etc., by hydrogen, at the ordinary pressure or at pressures up to two or three atmospheres and at temperatures between 25° and 45°. Hydrogenation of the cinchona alkaloids, although presenting greater difficulties, can also be effected in this way. According to the character of the treatment quinine or dihydroquinine is converted into hexahydrocinchonidine and dodecahydrocinchonidine. The same hexahydro-compound was also obtained by reduction of dihydrocinchonidine. Similarly, by hydrogenation of quinidine and cinchonine a hexahydrocinchonine was prepared.[1]

The suboxides of nickel, copper, iron, or cobalt may also be used as catalysts of hydrogenation in aqueous or alcoholic solutions of unsaturated compounds. For example, quinine hydrochloride, morphine, and cinnamyl-cocaine undergo reduction when treated with hydrogen in presence of these substances.[2]

In an alternative method for the reduction of alkaloids the use of free hydrogen is dispensed with, the reducing agent being nascent hydrogen liberated by the decomposition of formic acid in presence of finely divided metals of the platinum group ($HCOOH = H_2 + CO_2$). For example, 100 parts of a 2 per cent. solution of formic acid are added to 20 parts of quinine bisulphate and then 0·4 part of platinum black introduced. Decomposition of the formic acid begins at once, and when the evolution of the carbon dioxide has ceased the liquid is filtered and neutralized with ammonia; on cooling the sulphate of dihydroquinine separates. In a similar manner morphine, codeine, and the other opium alkaloids may be converted into dihydro-derivatives.[3]

Hydrogenation of Oils ("*Hardening of Fats*").[4]

Of late years the demand for hard fats has been considerably greater than the natural supply, and consequently

[1] Skita and Brunner, *Ber.*, 1916, **49**, 1597.

[2] Eng. P. 21883 and 21948 (1914).

[3] *Ibid.* 10204 (1913) and 14247 (1913).

[4] For detailed information on this subject readers are referred to Carleton Ellis's book, *The Hydrogenation of Oils* (1914).

any satisfactory method for the conversion of oils or liquid fats into solid fats is of great industrial importance.

The solid fats are chiefly composed of tripalmitin and tristearin, the glycerides of the saturated palmitic and stearic acids respectively, whereas in fatty oils and liquid fats there is a preponderating proportion of triolein, the liquid glyceride of the unsaturated oleic acid. Theoretically the transformation of liquid oleic acid into solid stearic acid is an extremely simple process, consisting in the addition of two atoms of hydrogen to the molecule of the former: $CH_3 \cdot (CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_7 \cdot COOH + H_2 = CH_3 \cdot (CH_2)_{16} \cdot COOH$. Equally simple is the conversion of the liquid glyceride triolein into the solid glyceride tristearin:—

$$C_3H_5(OOC \cdot C_{17}H_{33})_3 + 3H_2 = C_3H_5(OOC \cdot C_{17}H_{35})_3.$$

For many years chemists have sought for commercial methods for the preparation of valuable solid fats from relatively cheap materials such as whale oil, fish oils, etc., of which the use was necessarily more or less limited; for instance, the loathsome taste and smell of whale oil rendered it unfit for food or for soap making, although, of course, it could be used as a source of glycerol. It is, however, only within the last twenty years that practical methods of hardening oils have been discovered, and these are based on the discovery by Sabatier and Senderens that unsaturated compounds can be hydrogenated by treatment with hydrogen in presence of nickel or of other metals possessing catalytic activity.

The first patent[1] dealing with the hydrogenation of oils in the liquid form claims that this may be effected by exposing the fat or the fatty acid in a liquid condition to the action of hydrogen and the catalytic substance. "For instance, if fine nickel powder obtained by reduction in a current of hydrogen is added to chemically pure oleic acid, then the latter heated over an oil bath, and a strong current of hydrogen is caused to pass through it for a sufficient length of time, the oleic acid may be completely converted into

[1] Eng. P. 1515 (1903).

stearic acid. The quantity of the nickel thus added and the temperature are immaterial, and will only affect the duration of the process. Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute acids, the reaction passes off without any secondary reaction taking place. The same nickel may be used repeatedly. Instead of pure oleic acid commercial fatty acids may be treated in the same manner. The same method is applicable not only to free fatty acids but also to their glycerides occurring in nature, that is to say, the fats and oils. Olive oil will yield a hard tallow-like mass; linseed oil and fish oil will give similar results. By the new method all kinds of unsaturated fatty acids and glycerides may be easily hydrogenized. It is not necessary to employ pure hydrogen for the purpose of the present invention; commercial gas mixtures containing hydrogen, such as water gas, may be used."

Several of the statements made in this claim stand in need of correction, and the following points may be noted. As has been pointed out already the activity of a metallic catalyst depends very largely upon the way in which it is prepared, and therefore it is of importance to select methods of preparing the nickel or other metal to be used which will yield a very pure product in a suitable physical condition. Moreover, both the catalyst itself and the hydrogen, or mixture of gases containing hydrogen, employed in the process must be most carefully freed from such impurities as destroy the activity of the catalyst. The poisons most to be feared are sulphur, phosphorus, and arsenic and their volatile compounds, chlorine and the other halogen elements, ammonia and oxides of nitrogen, oxygen, which oxidises the catalyst and impairs its activity, and the empyreumatic substances formed in the preparation of water gas. In addition, the quantity of catalyst employed has a decided influence on the results of the operation. With each catalyst there is a certain quantity which gives the best results, and which must be determined by experiment in each case. For instance, in experiments with linseed oil

containing 0·5 per cent. of nickel there was practically no absorption of hydrogen even at a temperature of 250°; with 1 per cent. of the catalyst absorption was slow at 180°, and increased rapidly as the temperature was raised to 250°; with 5 per cent. of nickel absorption at 180° was much greater than with 1 per cent. at 250°.

As regards the temperature at which the process is carried on, it is generally the case that addition of hydrogen to an unsaturated compound can only be brought about effectively within a well-defined range of temperature, and that somewhere within this range lies the temperature at which saturation takes place with maximum velocity. For a number of fatty oils this temperature is approximately 180°, when nickel is the catalyst. The velocity of the reaction falls when the temperature is raised above this point, but less rapidly than when it is lowered. Hence in operation on the large scale it is better to maintain the temperature slightly above rather than below the point of greatest velocity, unless the character of the oil necessitates working at as low a temperature as possible. Rapidity of treatment is specially desirable in the case of edible oils, when prolonged contact with the catalyst introduces the danger of solution of the metallic material to an objectionable degree. The range of temperature varies with each catalyst; platinum and palladium in certain forms may be used below 100°, nickel between 160° and 200°, oxide of nickel and copper at about 200° and upwards; much, of course, depends upon the physical state of the catalyst.

Contrary to a very general opinion, it does not appear necessary that the mixture should be violently agitated in order to bring the catalyst into contact with the hydrogen, for once the catalyst is wetted with the oil there can be no actual contact with the gas. Apparently the hydrogen reaches the catalyst by dissolving in the oil. On the other hand, agitation of the mixture secures the rapid replacement of more saturated by less saturated portions of the oil.

The use of nickel in a number of different forms has been protected; these include nickel powder, nickel in the form

of extremely thin films or plates, nickelized asbestos, nickel deposited on pumice or other indifferent support, kieselguhr or other inert pulverulent carrier impregnated with nickel, and wood charcoal incorporated with or coated with the metal. An interesting method [1] for the production of a very pure and active form of the nickel depends upon the decomposition of nickel carbonyl ($Ni(CO)_4$) into nickel and carbon monoxide. This compound, which is prepared by the action of carbon monoxide on reduced nickel at a low temperature, is soluble in oil, and is very readily taken up by gases, and undergoes decomposition when heated to about 200°. In applying the compound on the practical scale, carbon monoxide is passed through a tube containing finely divided nickel and then into the oil, which is maintained at a temperature of about 180°. After sufficient of the catalyst has been formed by decomposition of the carbonyl, the current of carbon monoxide is cut off, the temperature raised to 220°–240°, and hydrogen then introduced.

According to a modified form of this process [2] hydrogen containing from 5 to 10 per cent. of carbon monoxide, which may easily be prepared from water gas, is passed over reduced nickel, which need not be pure but may be such a mixture as is obtained in the reduction of nickel ores. The mixture of hydrogen and any desired proportion of nickel carbonyl thus produced is passed into the substance to be hydrogenated at a temperature between 220° and 240°, when the carbonyl is decomposed with liberation of a particularly active form of nickel. The proportion of carbonyl required is very small, excellent results having been obtained with a quantity corresponding with 0·1 part of nickel in 100 parts of oil. Fresh quantities of the carbonyl are always passing into the oil, and the nickel appears to act in the nascent condition at the moment of decomposition of that compound. It is claimed that this process offers great technical advantages over the preceding one, in so far that the liberation of nickel occurs in presence of the hydrogen and the oil.

[1] D. R. P. 241823. [2] Eng. P. 18988 (1912).

Not only nickel itself, but oxide of nickel or other metallic oxides may be used as catalysts, in quantities amounting to about 1 per cent. of the weight of the oil. In this case the hydrogen may be employed either alone, or mixed with oxygen or air, and a higher temperature than the usual, viz. about 250°, is recommended.[1] In another process [2] a metallic compound, for example nickel carbonate, is reduced by hydrogen under such conditions that the metal in the product exists, as far as possible, in the form of one or more suboxides. The product of the reduction of nickel carbonate is more active as a catalyst the lower the temperature of reduction; a range of temperature between 230° and 270° appears to be the most suitable. The product may be collected for immediate use in the oil to be hydrogenated, or it may be collected in water, filtered, dried in air, and then prepared for use by heating in hydrogen for one to two hours at 180°. The suboxide catalyst may also be prepared by heating finely divided reduced nickel in air or oxygen diluted with carbon dioxide at a temperature between 300° and 400°.

Bedford and Erdmann [3] point out that the hydrogenation of oils with finely divided nickel has the disadvantage that the catalyst is sensitive to small quantities of air and to traces of chlorine and of sulphur compounds, of which the latter may be developed from the protein always present in both vegetable and animal oils. They have found, however, that the oxides of nickel are capable of acting as hydrogen carriers at atmospheric pressure, and possess the advantage over nickel of being relatively insensitive to gases containing oxygen and compounds of sulphur; moreover, the hydrogenation proceeds with much greater velocity than with nickel. With the higher oxides a temperature of about 250° is required, but with the suboxide 180°–200° is sufficient. When the higher oxides are used they become partially reduced to the suboxide, which forms a colloidal suspension in the oil; hence a nickel oxide catalyst becomes

[1] U.S. P. 1026339. Eng. P. 4702 (1912).

[3] *J. pr. Chem.*, 1913, **87**, 425.

more active after it has been used. No reduction of the oxide to metallic nickel occurs during the process, although in absence of oil this begins to take place at 190°. Nickel soaps are formed only to a slight extent. Other oxides, for example, cupric oxide and ferrous oxide, are capable of acting as catalysts, but are not so efficient as nickel oxide; the activity of the latter is increased by the addition of small quantities of the oxides of aluminium, silver, zirconium, titanium, cerium, lanthanum, or magnesium.

In connection with the statement that the metallic oxide used as catalyst does not undergo reduction to metal during the process of hydrogenation, it should be noted that some chemists hold a different opinion. Thus Normann and Prings [1] have found that various unsaturated oils are readily hardened by hydrogen at temperatures between 200° and 250° in presence of the oxide, hydroxide, carbonate, or formate of nickel, added in the proportion of 1 per cent. of the weight of the oil; but that in each case the formation of metallic nickel takes place. On the average the catalyst after hydrogenation was proved to contain from 4 to 7 per cent. of the metal. Rapid hardening was also effected by means of a nickel-kieselguhr mixture, prepared by reduction at 500° and containing about 4 per cent. of the metal.

Other proposed catalysts include nickel, cobalt, copper or iron salts of organic acids, *e.g.* the formates, acetates, or lactates,[2] and soaps of heavy metals or of noble metals made from a fat or a fatty acid having a higher melting point than that of the saturated compound to be produced.[3]

The rarer metals or their compounds have also been pressed into the service of the oil chemist. One patent [4] recommends platinum or palladium chlorides ($PtCl_2$, $PtCl_4$, H_2PtCl_6, K_2PtCl_6, $PdCl_2$, etc.) mixed with a neutralizing agent such as anhydrous Na_2CO_3 to prevent the formation of free acid. The salts in the state of powder are mixed with the fats or fatty acids, and hydrogen is allowed to act on the mixture, which is continuously stirred, at temperatures below 100°

[1] *Chem. Zeit.*, 1915, **39**, 29, 41.
[2] U.S. P. 1081182.
[3] Eng. P. 18310 (1912).
[4] U.S. P. 1023753.

and preferably under a pressure of several atmospheres. The salts may also be used in conjunction with the platinum metals deposited on carriers devoid of anticatalytic action such as copper or magnesium carbonate. In a short time the solid hydrogenation product is obtained. Very small quantities of the salts, which must be present in the solid form during the progress of the reaction, are sufficient to bring about the reduction of large quantities of fats or fatty acids by hydrogen; for example, 1·7 parts of palladium chloride, equivalent to 1 part of palladium, in presence of hydrogen will convert 10,000 parts of fat or fatty acids into solid masses within three or four hours. When reduction is completed the platinum metals or their compounds can be easily separated and used again.

The time required for the reduction depends upon the amount of the salt added and the pressure under which the hydrogen is caused to act. The following example of the method may be quoted: 1,000,000 parts of castor oil or of oleic acid are mixed with 34 parts of dry $PdCl_2$ (= 20 parts of Pd), or with 140 parts of dry $PtCl_2$ (= 100 parts of Pt), or 172 parts of $PtCl_4$, or 230 parts of H_2PtCl_6, in each case with or without the equivalent quantity of anhydrous Na_2CO_3. The mixture is placed in a pressure vessel from which the air is exhausted as completely as possible, and hydrogen is then admitted under a pressure of two or three atmospheres. The mixture is kept in motion by stirring apparatus, and the vessel heated to a temperature of about 80°, although reduction may also be carried out at lower temperatures. When the pressure gauge indicates only a low pressure, more hydrogen is admitted; when the gas pressure remains constant for a considerable period the reaction is complete. The reduction product is freed from the catalyst in a filter press which can be heated.

Patents have also been taken out covering the use of aqueous solutions of compounds of metals of the platinum group, usually with addition of hydrochloric acid;[1] of the metals iridium, rhodium, ruthenium and osmium, either in the

[1] U.S. P. 1063746.

metallic state or in the form of a lower hydroxide;[1] of mixtures of oxides, hydroxides, or carbonates of two or more of the metals nickel, cobalt, copper, or iron, or of one or more of these with finely divided platinum, palladium, or silver, or with silver oxide, which when mixed with the oil enable reduction and hydrogenation to be effected simultaneously at lower temperatures than hitherto possible;[2] of catalysts of greasy consistency containing inorganic metallic colloids, prepared by incorporating solutions of divalent salts of metals of the platinum group with such substances as wool fat or the alcohols obtainable therefrom, and adding an alkali carbonate to form the colloidal lower hydroxide of the metal; instead of alkali carbonates alkali salts of the higher fatty acid (*i. e.* soaps) may be used.[3]

Since liquid fats and fatty acids are essentially cheaper than solid fats or fatty acids, the ability to prepare from the former a fatty body of almost any desired degree of consistency or hardness renders hydrogenation a process of great importance for the production of edible fats and of materials for soap making and for purposes of lubrication. As regards edible fats, the addition of less than 1 per cent. of hydrogen suffices to convert cotton-seed or other vegetable oils (*e. g.* palm-kernel, soya-bean, pea-nut oils) into a fatty body of at least the consistency of lard, and the product from cotton-seed oil has the advantage of being very stable in character. The oil may be directly hardened to the consistency of lard, care being taken to employ an oil as nearly neutral as possible in order to prevent dissolution of the catalyst, and to avoid a high temperature during the process, so as not to impair the flavour; or, alternatively, a large proportion of the original oil may be thickened by admixture of a small quantity of a relatively hard hydrogenation product. So far as digestibility is concerned, even whale oil appears to be fit for use as a food after being hardened. At the same time a point which requires consideration is that an oil hardened by a process involving the use of nickel as a catalyst always

[1] Fr. P. 425729. [2] Eng. P. 12981 and 12982 (1912).
[3] U.S. P. 1077891.

contains small quantities of the metal, and it is just possible that even these minute quantities—a few milligrammes per kilo of fat—might produce injurious effects.

As regards soap making the great advantage of the hydrogenation process is that materials which formerly could only be used for the preparation of soft soaps can now be converted into materials from which hard soaps can be produced. Even fish oils and whale oil are available for this purpose, because they can be completely deodorized by the action of hydrogen. Moreover, hardened oils seem likely to be used largely in the future for lubricating purposes, and in the tanning industry stearin produced by hydrogenation is being employed instead of oleo-stearin.

Hydrogenation accompanied by Decomposition.

In the hydrogenation of unsaturated compounds in the state of vapour, with nickel as the catalyst, the metal frequently promotes another kind of change, namely the decomposition of the molecules of the original substance into simpler molecules or groups of atoms which in turn may unite with hydrogen, or even, when the temperature is high enough and the proportion of hydrogen in the system small, into carbon and hydrogen. This effect always occurs during the hydrogenation of hydrocarbons of all classes if the temperature is sufficiently high, and in general at temperatures above 300°. Even benzene and other cyclic hydrocarbons tend to break down at temperatures of 300°–350° into smaller molecules, principally methane.

When acetylene is hydrogenated in the cold or at low temperatures, the production of ethane is accompanied by that of small quantities of higher gaseous or liquid hydrocarbons. This is probably due to the acetylene being broken down into CH groups, which by union with hydrogen form CH_4, CH_3 or CH_2 groups; these in turn can unite with each other in a variety of ways. By carrying out the reaction at 200° for a considerable time Sabatier and Senderens obtained a liquid consisting principally of pentane and its homologues together with small quantities of olefines and traces of aromatic

hydrocarbons. In its composition, and also in density, odour, and fluorescence this liquid closely resembled Pennsylvanian petroleum. By passing acetylene unmixed with hydrogen through a tube containing reduced nickel and maintained at a temperature between 200° and 300°, the same observers obtained another liquid consisting principally of hydroaromatic hydrocarbons, and very similar in character to Caucasian petroleum. On these facts they have formulated a theory of the formation of natural petroleums. Assuming that in the interior of the earth large masses of the alkali and alkaline earth metals exist, together with the carbides of these metals, and that these substances come into contact with water vapour, hydrogen and acetylene respectively would be formed. If the mixture of gases contained hydrogen in large excess, then on its coming into contact with nickel, cobalt, or iron at temperatures lower than 200° American petroleum would be formed together with large quantities of combustible gases (hydrogen, methane, ethane, etc.), such as are met with at Pittsburg. If the acetylene contained only a small proportion of hydrogen there would result principally hydroaromatic hydrocarbons, or Caucasian petroleum. Intermediate conditions would give rise to the petroleums of Galicia or Roumania.

CHAPTER V

Dehydrogenation

Those metals which catalyse the combination of hydrogen with other substances are also capable, under different conditions of temperature, of exercising catalytic influence in promoting the opposite reaction of dehydrogenation. Thus it has been known for long that iron, copper, gold, silver, and platinum greatly accelerate the thermal decomposition of ammonia into its elements, and that the temperature at which acetylene breaks down into carbon and hydrogen is greatly reduced if the reaction is carried out in presence of spongy platinum, or of reduced iron, cobalt, or nickel.

The most efficient catalysts of dehydrogenation are the active metals, and in a lesser degree certain metallic oxides and salts, among which anhydrous aluminium chloride occupies a prominent position; carbon also is a catalyst in reactions of this kind.

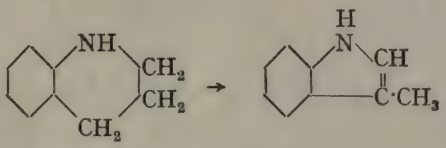
The reactions of dehydrogenation brought about with the aid of such catalysts may be classified in four groups :—

(1) The regeneration of cyclic compounds from their hydrogenated derivatives, or the formation of other unsaturated hydrocarbons, by loss of hydrogen.
(2) The degradation of hydrocarbons.
(3) The production of aldehydes and ketones from primary and secondary alcohols respectively.
(4) The formation of cyclic compounds through loss of hydrogen.

Dehydrogenation of Hydrocyclic Compounds.

The regeneration of the more stable cyclic compounds from the products obtained from them by hydrogenation takes

place more or less readily if the latter substances are heated to sufficiently high temperatures, and is greatly assisted by the catalytic action of reduced metals, particularly nickel. In presence of this metal cyclohexane and its homologues and derivatives, for example, cyclohexanol and cyclohexylamine, begin to lose hydrogen at temperatures above 270° with formation of benzene or a corresponding derivative of benzene; as a rule the hydrogen set free reacts with a portion of the hydrocarbon in such a way that methane or other simpler hydrocarbon is also produced: *e.g.* $3C_6H_{12} = 2C_6H_6 + 6CH_4$. The hydrides of naphthalene and other complex hydrocarbons behave in a similar manner; piperidine between 180° and 250° is completely converted into pyridine, even in presence of hydrogen; tetrahydroquinoline at 180° yields a certain quantity of quinoline but is for the most part transformed into scatole :—



Palladium black is a very energetic catalyst in the dehydrogenation of the hydroaromatic compounds; the reaction is vigorous at 200° and reaches a maximum at 300°. On the other hand, cyclopentane and its derivatives and also cycloheptane do not undergo dehydrogenation below 300°. According to Zelinsky [1] catalytic dehydrogenation by palladium or platinum at a temperature of about 300° appears to be characteristic of cyclohexane and its homologues (hydroaromatic hydrocarbons), and the reaction may be applied to the separation of hydrocarbons of the cyclopentane and cyclohexane series and to the investigation of petroleum distillates. In order to test this, a mixture of methylcyclopentane and cyclohexane was subjected three times in succession to the action of platinum black at 300°. The quantity of hydrogen evolved was 93·4 per cent. of the

[1] *Ber.*, 1912, **45**, 3678.

theoretical quantity calculated for the conversion of the cyclohexane into benzene. The product was treated with sulphuric acid containing a little sulphuric anhydride, which sulphonated the benzene, and the residual hydrocarbon after distillation over sodium was found to have all the properties of methylcyclopentane.

As an example of the formation of an unsaturated hydrocarbon by dehydrogenation, the conversion of 1 : 2-butylene into butadiene [1] may be quoted :

$$CH_3 \cdot CH_2 \cdot CH : CH_2 = CH_2 : CH \cdot CH : CH_2 + H_2.$$

The butylene is passed during one hour through a tube containing copper heated to redness. The mixture of butadiene and unchanged butylene is condensed, the butadiene polymerized to rubber by means of metallic sodium, and the butylene recovered by heating.

Butadiene (erythrene) can also be obtained by the action of heated catalysts on cyclohexane, its homologues or derivatives, the dehydrogenation in this case being accompanied by breaking down of the molecule of the cyclic compounds. The vapours of cyclohexane are passed over a spiral of aluminium silicate heated electrically to a dull red heat, and the unchanged hydrocarbon returned to the boiler, whilst the gases are freed by cooling from liquid hydrocarbons and the erythrene extracted by physical or chemical means.[2]

Partially saturated cyclic hydrocarbons are obtained with good yields when halogen derivatives of hexahydrobenzene or other hydrocyclic hydrocarbons are passed in the state of vapour over heated substances capable of removing hydrohalogen acids, or suitable catalytic agents. The reaction may be carried out under the ordinary or reduced pressure, and it is advisable to use temperatures lower than those at which the desired hydrocarbons decompose. As catalytic agents barium chloride, alumina, nickel chloride, etc., may be employed. Thus monochlorocyclohexane is converted

[1] Eng. P. 9722 (1911). [2] *Ibid.* 448 (1912).

into tetrahydrobenzene, dichlorocyclohexane into dihydrobenzene, and chloropentamethylene into cyclopentene.[1]

Degradation of Hydrocarbons.

The process of dehydrogenation which occurs when hydrocarbons in general are heated in presence of metallic catalysts is accompanied by a more or less extensive decomposition of the original compounds into radicles which are capable of uniting with each other in various ways to form other hydrocarbons containing smaller proportions of hydrogen; but at the same time the more complex hydrocarbons such as benzene, naphthalene, etc., which may be produced in this way are themselves liable to undergo decomposition into simpler substances or ultimately into carbon and hydrogen. Among the metallic catalysts nickel as a rule produces the most intense effects.

When in contact with reduced nickel methane yields an appreciable deposit of carbon when the temperature reaches 390°, and ethane begins to decompose at 325° into methane, hydrogen, and carbon. Ethylene at temperatures above 300° is completely decomposed into a voluminous mass of carbon and a mixture of hydrogen, methane, and ethane, the proportions of the last becoming smaller the higher the temperature of the metal. Cobalt and iron have an effect similar to nickel, but are less active.

Acetylene is rapidly broken down into carbon and hydrogen when passed over platinum black heated to 150°. The heat liberated causes incandescence of the metal, which on the one hand accelerates the decomposition, and on the other hand promotes the polymerization of part of the acetylene into benzene and other more complex hydrocarbons; the hydrogen liberated may also convert part of the acetylene into ethylene or ethane.

Even at the ordinary temperature reduced iron induces vigorous decomposition of acetylene; the reaction is chiefly confined to the formation of carbon and hydrogen, but a

[1] Fr. P. 441203.

small quantity of a liquid product composed almost exclusively of aromatic hydrocarbons can be condensed; the gas which escapes condensation is a mixture of hydrogen, some unchanged acetylene, and some benzene vapour. If, on the other hand, the metal is maintained at a temperature above 180° the escaping gas contains some ethane, some ethylene, etc., and a larger proportion of liquid products is condensed.

The mode of action of copper is different. When a current of acetylene is passed over reduced copper, heated above 180°, it is rapidly absorbed, and only after some time does any gas pass through. The copper appears to swell up and soon obstructs the tube, becoming mixed with a brown solid. The escaping gas contains a little acetylene, some ethylene and other olefines, and some ethane; the liquid product is a mixture of olefines and aromatic hydrocarbons. If the brown solid is treated several times with acetylene, until no further change occurs, a yellow compound, cuprene, of the formula $(C_7H_6)_n$ is finally obtained.

With nickel at the ordinary temperature the behaviour of acetylene is much the same as with iron. At a temperature of about 180° the action of nickel on acetylene has a threefold result: firstly, rapid decomposition to carbon and hydrogen, with simultaneous polymerization of a portion of the acetylene into aromatic hydrocarbons; secondly, slow condensation of the acetylene into a solid hydrocarbon which appears to be identical with cuprene; and lastly hydrogenation of the acetylene and of its polymerization products with formation of paraffins, olefines, and hydroaromatic compounds.

Some at least of the reactions just referred to find applications in one or other of the processes for the "cracking" of petroleum, that is to say, for the production from heavy oils of light oils with comparatively low boiling points suitable for use in internal combustion engines.

The Cracking of Petroleum.[1]

The products of the pyrogenetic treatment of petroleum fall into four groups—permanent gas, illuminating oils, aromatic hydrocarbons, and volatile fuels for internal combustion engines. The proportions in which these different products are formed depend very largely on the temperature and the pressure at which the cracking process is carried out. Alteration in temperature affects not only the velocity of the various reactions involved, but also, and in a marked degree, the character of the products. In the majority of modern systems for the cracking of petroleum it has been found that at temperatures of about 500° the tendency is toward the formation of a mixture of paraffins and olefines, whereas at higher temperatures, about 700°, the effect is the generation of aromatic compounds. The general effect of increased pressure is to favour the synthesis of more complex hydrocarbons, whilst diminished pressure promotes the decomposition of more complex into simpler compounds.

The influence of catalysts in such reactions as the hydrogenation, the dehydrogenation, the decomposition, and the condensation of hydrocarbons has been the subject of many investigations, which had their origin in the classic work of Sabatier and Senderens. It may be recalled that those observers have shown that when mixtures of ethylene and hydrogen are passed over finely divided nickel at a temperature of 300°, the product is chiefly methane, whilst at a lower temperature ethane is formed. They have also shown that when mixtures of acetylene and hydrogen are passed over finely divided nickel, copper, iron, or cobalt at moderately low temperatures liquid mixtures containing paraffins, olefines, and aromatic hydrocarbons are produced along with ethylene and ethane; that the proportion of liquid hydrocarbons produced increases with the temperature, and that an increase in the proportion of acetylene employed leads to

[1] *See* an exhaustive paper on "The Pyrogenesis of Hydrocarbons," by Lomax, Dunstan, and Thole, *J. Inst. Petrol. Tech.*, 1916, **3**, 36.

an increase in the amount of aromatic hydrocarbons formed; that under similar conditions mixtures of ethylene and hydrogen yield products of a similar character; and that the character of the liquid products can be changed by varying the proportions of the gaseous hydrocarbon and the hydrogen as well as by alteration of the temperature of the reaction. Finally, they showed that aromatic hydrocarbons could be hydrogenated in presence of such catalysts as nickel at temperatures below 250°, whilst above that temperature, and especially towards 300°, the reverse action, dehydrogenation, sets in.

This work led to many investigations on the influence of various catalysts on hydrocarbons of different groups, either alone or in presence of hydrogen, at the ordinary pressure or at pressures increased even up to 220 atmospheres, and at various temperatures. Among the catalysts employed are metals, *e.g.* iron, cobalt, nickel, aluminium, and platinum; metallic oxides such as alumina and titanium dioxide; aluminium chloride, kaolin, fuller's earth, etc. Since 1906 many patents for the production of light spirits from petroleum by the action of catalysts have been filed, a few of which may be quoted.

In 1908 Sabatier patented [1] a process for the production of a light spirit boiling below 150°, which consisted in passing the vapours of heavy oils over finely divided metals at a dull red heat, and then hydrogenating the product of this reaction, which consisted mainly of unsaturated hydrocarbons, in presence of finely divided nickel at 150°–300°. According to a later modification [2] the vapours of the heavy oils are decomposed by passage either over a network of wires heated electrically from 500° to a red heat, or over a catalyst composed of finely divided metals or metallic oxides, *e.g.* oxide of iron, or salts capable of reduction to metal, mixed with a neutral refractory substance free from silica, such as magnesia, alumina, or graphite, and an agglutinant also free from silica, for example, glue, dextrin, or starch, and maintained at a temperature of 300° by an electric

[1] Fr. P. 400141. [2] *Ibid.* 475303.

current. The unsaturated hydrocarbons produced are subsequently converted into saturated compounds by hydrogenation over finely divided nickel at 200°–300°. When the catalyst becomes coated with carbon it is regenerated by heating in a current of steam.

Hall's process [1] consists in heating the vapours of heavy hydrocarbons at a temperature of 600° and upwards and under a pressure of 5 atmospheres in presence of a catalyst capable of affixing hydrogen, allowing the vapours to expand and deposit carbon, and then condensing them. The catalysts specified are metals such as nickel, cobalt, silver, palladium, chromium, and manganese, or their oxides.

It is claimed [2] that benzene can be obtained by passing the vapours of petroleum together with hydrogen through a tube containing catalytic materials heated to a temperature between 180° and 300°. Suitable catalysts are iron, copper, zinc, aluminium, nickel, cobalt, silver, and platinum, or mixtures of those metals.

In another process [3] the oil is distilled in a separate still, and the vapours to be cracked are passed through a tube packed with the catalyst and then through fractionating and condensing plant. Part of the uncondensed gas is passed through an ammonia saturator under slight pressure to the still, where it is sprayed over the surface of the oil; this helps to carry the oil vapour to the cracking tube and incidentally reduces the temperature of distillation. It is stated that a portion of the ammonia is dissociated, and that the nascent hydrogen in presence of the catalyst hydrogenizes a part of the unsaturated hydrocarbons present and appears also to arrest the separation of carbon. The ammonia also tends to produce a spirit free from sulphur even when an oil containing 5 or 6 per cent., such as Mexican oil, is used. The catalyst is made by heating a metallic oxide or mixture of oxides with organic compounds, *e. g.* oxalates or tartrates, of the metal.

A different method [4] of obtaining light spirit is to bring

[1] Eng. P. 17121 (1913). [2] *Ibid.* 17272 (1913).
[3] *Ibid.* 20470 (1913); 2838 (1914). [4] *Ibid.* 5434 (1914).

mineral oils or residues, in the liquid state, into contact with quicklime, or quicklime containing carbon, at temperatures between 400° and 650°. According to another patent [1] a mixture of the vaporized oil and steam is passed over oxide of iron, or of another metal capable of forming several oxides, at 500°–600°. This catalyst may be regenerated, when the production of light hydrocarbons begins to diminish, by heating in a current of air.

The use of aluminium chloride as a catalyst for the production of motor spirit from heavy oils is claimed in a number of different patents. As an example, the process described by McAfee [2] may be quoted. The oil freed from water and lighter constituents is distilled with anhydrous aluminium chloride in a still provided with a stirrer at a temperature of about 260°–290°. The process usually occupies from 24 to 48 hours. Constituents of high boiling point and volatilized aluminium chloride are separated from the vapour in two air-cooled condensers connected in series and are returned to the still, and the vapours at a temperature of about 175° pass finally to a water-cooled condenser. The products are stated to be saturated and to require no treatment with sulphuric acid; they are freed from sulphuretted hydrogen by washing with alkali and water. The yields of gasoline from Cuddo and Oklahoma oils are stated to be 43·3 per cent. and 34·8 per cent. respectively, as compared with yields of 18 per cent. and 12·5 per cent. obtained by the ordinary cracking process. The aluminium chloride is recovered from the residual coke by treatment with chlorine at a red heat.

Suitable catalytic bodies for the production of light from heavy hydrocarbons are obtained, it is claimed,[3] by heating a powdered metallic oxide or mixture of oxides with organic compounds of the metal. For instance a mixture of 32 parts of ferric oxide, 7·5 parts of nickel oxide, 5·5 parts of carbon, 14 parts of ferrous oxalate, and 15 parts of nickel oxalate is incorporated with 17·5 per cent. of its weight of

[1] Eng. P. 11420 (1914).
[2] *J. Ind. and Eng. Chem.*, 1915, **7**,737.
[3] Eng. P. 5847 (1914).

tar, briquetted and sintered in a closed crucible at a temperature below the melting point of the metals. Other catalytic metals such as chromium, cobalt or manganese may be used, and the addition of small amounts of aluminium, cerium magnesium or other members of the alkaline earth group is an advantage in many cases. The catalytic bodies so produced do not appear to lose their efficiency under continued use; in fact, in some cases the efficiency of the catalyst appears to increase after a short period.

The Dehydrogenation of Alcohols.

Many years ago Berthelot observed that the vapour of ethyl alcohol, when passed through a heated glass tube, begins to decompose at about 500°, two reactions taking place simultaneously, namely, (1) dehydration of the alcohol, with the formation of water and ethylene, and (2) dehydrogenation, resulting in the production of hydrogen and acetaldehyde :—

(1) $CH_3 \cdot CH_2OH = CH_2 : CH_2 + H_2O.$

(2) $CH_3 \cdot CH_2OH = CH_3 \cdot CHO + H_2.$

The reaction under these conditions is complicated by the effect of the higher temperature on the ethylene and the acetaldehyde, the latter in particular being partially decomposed into methane and carbon monoxide.

Other primary alcohols undergo similar reactions at a low red heat; no appreciable change occurs at temperatures below 400°.

Secondary alcohols are more readily affected by exposure to high temperatures, dehydration yielding hydrocarbons, and dehydrogenation ketones; one or other reaction predominates according to the character of the alcohol; *e. g.* :—

(1) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH = \begin{matrix} CH_3 \\ CH_2 \end{matrix}\!\!>\!CH + H_2O.$

(2) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + H_2.$

In presence of catalysts these reactions can be brought about with greater velocity and at lower temperatures. The metals copper, cobalt, nickel, iron, zinc, platinum, and palladium, especially when in a finely divided state, act as catalysts of dehydrogenation, promoting the decomposition of the alcohols into hydrogen and aldehydes or ketones respectively. The same is true of a small number of metallic oxides, for instance, manganous oxide, but their activity is much less than that of the metals.

The conversion of the alcohol into the aldehyde or ketone is never complete, even when a long column of the catalyst is used, because the hydrogen liberated from the alcohol tends to reunite with the dehydrogenation product under the catalytic influence of the metal. If the temperature is raised above a certain point the aldehyde produced is partially decomposed into carbon monoxide and a hydrocarbon, for example, acetaldehyde is converted into methane and carbon monoxide : $CH_3 \cdot CHO = CH_4 + CO$. Except in the case of formaldehyde and of aromatic aldehydes, this decomposition does not take place to any marked extent below 300°.

Reduced copper is the most suitable of all the catalysts of dehydrogenation for the production of aldehydes or ketones by this method, and has been used for the preparation of acetaldehyde from ethyl alcohol on the large scale with very satisfactory results.

The vapour of alcohol is passed from a boiler through a tube of copper or brass filled with the catalyst and maintained at a temperature of about 300° by electrical heating,[1] or by heating in an air bath or even in a tube furnace. A convenient size of tube is 70–100 cm. long and 2 cm. in diameter. The temperature should not be allowed to fall much below 300°, but may be raised above this point, even up to 400°, as the catalyst begins to lose its activity. The catalyst consists of copper prepared by reduction of the oxide at a low temperature, or of pumice coated over with copper (*e.g.* by saturation with a solution of copper formate, drying,

[1] Cf. Bouveault, *Bull. Soc. Chim.*, 1908 (4), 3, 50, 119.

and reduction); a mixture of 5 parts of copper and 1 part of magnesium has also been recommended. The alcohol need not necessarily be absolute; even 85 per cent. alcohol gives a satisfactory yield. It is preferable that the alcohol vapour should be preheated to about 300° before coming into contact with the copper. The vapours issuing from the tube, when condensed by passage through a condenser cooled with ice water, yield a mixture of unchanged alcohol, a little water, and acetaldehyde, containing up to 40 per cent. of aldehyde; the escaping hydrogen carries with it a certain proportion of the aldehyde, which may be recovered by passing the gas through a long worm cooled by a freezing mixture, or through absorption vessels charged with alcohol. The aldehyde is separated from the condensed liquid by fractional distillation; with the aid of an efficient fractionating column two distillations are usually sufficient to give a pure product. The alcohol residues from which the aldehyde has been separated always contain traces of acid which impairs the efficiency of the catalyst, and consequently should be made neutral by addition of alkali, and redistilled before being again passed through the catalysing tube. In any case the copper loses its activity after some time, but is easily regenerated by oxidation in a current of air at 300°, and subsequent reduction of the oxide with hydrogen or alcohol vapour.

The transformation of secondary alcohols into ketones by the catalytic action of finely divided copper is effected still more easily than that of primary alcohols into aldehydes, because owing to the superior stability of the ketones under the conditions of the reaction it is possible to work at higher temperatures without introducing complications. The yield of ketone may exceed 75 per cent. of the theoretical amount. Among the suggested applications of this process, is the preparation of camphor from borneol. The reaction takes place rapidly and almost quantitatively in presence of reduced copper at a temperature of 300°.[1]

The reaction may also be used to distinguished primary,

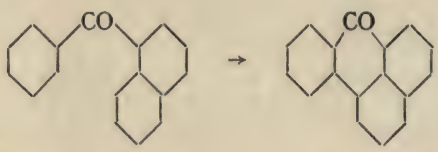
[1] Eng. P. 17573 (1906).

secondary, and tertiary alcohols from each other, the products of dehydrogenation being aldehydes, ketones, and unsaturated hydrocarbons respectively.[1]

Formation of Cyclic Compounds through elimination of Hydrogen.

Instances of the acceleration, through the catalytic influence of anhydrous aluminium chloride, of certain condensations of aromatic nuclei have long been known, and the reaction has been found to be a fairly general one with certain types of compounds. Thus when aromatic ketones are heated with that catalyst at temperatures between 80° and 140° condensation usually takes place, especially in cases where the elimination of hydrogen leads to the formation of new rings.

When phenyl-α-naphthyl ketone is heated with aluminium chloride benzanthrone is obtained in good yield and in a state of great purity. Hydrogen is evolved only to a small extent, most of that produced acting as a reducing agent on the reaction product; this reducing action, however, is counteracted in many cases by atmospheric oxidation accelerated by the aluminium chloride.



Under similar conditions *o*-, *m*-, and *p*-tolyl α-naphthyl ketones yield respectively 5-,6-, and 7-methylbenzanthrones. When melted with alcoholic potash the two former give 5:5′- and 6:6′-dimethylviolanthrones, which are vat dyes similar to violanthrone (Indanthrene Dark Blue B.O.). Other vat dyes can be obtained in a corresponding manner from the condensation products of other ketones.[2]

[1] Neave, *Analyst*, 1909, **34**, 346.
[2] Scholl and Seer, *Monatsh.*, 1912, **33**, 1.

Oxidation

A number of processes in which oxidation is effected either directly by means of oxygen, or indirectly through the action of oxidizing agents are induced or accelerated by various catalysts. The following are some typical examples.

Oxidation with Oxygen in presence of Catalysts.

Preparation of Formaldehyde.—A well-known example of direct oxidation with oxygen in the presence of a catalyst is the production of formaldehyde by passing a mixture of the vapour of methyl alcohol and air through a tube containing heated copper or platinum in the form of gauze or in a fine state of division: $2H{\cdot}CH_2OH + O = 2H{\cdot}CHO + H_2O$. The product, consisting of formaldehyde, water, and unchanged methyl alcohol is condensed and rectified in a still provided with a fractionating column.

Preliminary heating of the copper is unnecessary if some fragments of pumice stone coated with platinum or palladium (prepared by igniting the pumice after saturating it with a solution of a salt of the metal) is placed in front of it. The mixture of methyl alcohol vapour and air, heated to 100°, ignites in contact with the platinum and the copper spiral is thus caused to glow. The use of this "igniter" on the manufacturing scale is said to increase the yield of 40 per cent. formaldehyde by from 120 to 150 per cent. Pure metallic copper is not active as a catalyst when first used, but becomes so when the metal is superficially oxidized and has become more or less spongy through frequent use. The presence of platinum increases the activity of the copper, but lead has the opposite effect; in course of time the copper becomes inactive. In technical practice porous substances such as graphite, coke, etc., are used along with the copper. It is stated [1] that a quantitative yield of formaldehyde can be obtained from methyl alcohol by making use of a catalyst consisting of silver precipitated on asbestos.

A method which has been patented [2] for the preparation

[1] D. R. P. 228697. [2] *Ibid.* 286731.

of formaldehyde from methane consists in heating a mixture of methane with a large excess of air to a temperature between 150° and 220° in presence of a metal or a metallic couple: $CH_4 + O_2 = HCHO + H_2O$. For instance, a mixture of 3 parts of methane and 100 parts of moist air is passed over copper or silver or both heated to 150°–200°. The portion of the methane converted into formaldehyde is removed by treating the gaseous mixture with water, and the residual gas, after addition of a further quantity of oxygen to make up for that consumed, is again passed over the heated metal.

Preparation of Acetic Acid from Acetaldehyde,

$$2CH_3{\cdot}CHO + O_2 = 2CH_3{\cdot}COOH.$$

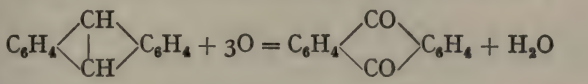
Acetaldehyde is submitted to oxidation in presence of acetic acid, or its chloro-derivatives, *e.g.* monochloroacetic acid, or acetic anhydride, or homologues of these compounds. Air or oxygen is introduced with brisk stirring into a mixture of 200 kilos of glacial acetic acid and 10–20 kilos of acetaldehyde, which is heated to a temperature between 70° and 100°, and when the greater part of the aldehyde, which is rapidly oxidized, has been converted into acetic acid, a further quantity is added and the oxidation proceeded with. The acetic acid may be distributed over a filling material in towers, and a mixture of aldehyde vapour and oxygen or air passed through the mass. The presence of a suitable catalyst, such as vanadium pentoxide, uranium oxide, or roasted ferroso-ferric oxide, greatly facilitates the reaction.[1]

In the process just described the acetaldehyde to be oxidized is mixed with a large proportion of acetic acid, but in another process the latter substance is dispensed with. In presence of small quantities of compounds of manganese the conversion of acetaldehyde into acetic acid is rapid, but the reaction does not take place with explosive violence as is the case when compounds of chromium, vanadium, cerium, etc., are used as accelerators. A current of dry oxygen is passed through a mixture of 300 kilos of pure

[1] Eng. P. 17424 (1911).

acetaldehyde and 2 kilos of manganous acetate contained in a vessel made of pure aluminium provided with a stirrer and a cooling jacket. The manganous salt dissolves in the acetaldehyde and the mixture absorbs oxygen very energetically, the heat evolved being removed by external cooling. After from ten to twenty hours the oxidation is complete, and the acid produced is distilled. Air may be used instead of oxygen, and the gas may be introduced under pressure; acetic acid or other solvent may be added to the acetaldehyde if desired.[1]

Preparation of Anthraquinone from Anthracene,



Anthracene, dissolved or suspended in a neutral or alkaline medium, is heated with oxygen under pressure in presence of a catalyst; cupric oxide is recommended, but compounds of nickel, cobalt, iron, or lead may be used in its place. For example, 100 parts of 30 per cent. anthracene paste are mixed with 3000 parts of water, 250 parts of 25 per cent. ammonia solution and 5 parts of cupric oxide in a vessel capable of withstanding pressure. A quantity of oxygen corresponding with three atoms per molecule of anthracene, or the equivalent quantity of air, is forced in, and the mass is stirred and heated for twenty hours at a temperature of 170°. After cooling the anthraquinone is separated and freed from copper compounds by washing with ammoniacal water.[2]

Preparation of Aniline Black.

In dyeing fabrics with Aniline Black the dye is produced on the fibre, and in order to avoid weakening of the fibre through the use of an oxidizing agent a process has been patented in which the oxidation of the aniline salt is effected by atmospheric oxygen.[3] The process depends upon the

[1] Fr. P. 460971. [2] D. R. P. 292681.
[3] Eng. P. (16189 1907).

discovery that the addition of a small quantity of a *p*-diamine or a *p*-aminophenol to a solution containing aniline or one of its homologues, an organic or mineral acid, and an oxygen-carrier, such as a copper salt, greatly accelerates the oxidation process. To prevent the formation of oxidation products in the "padding" liquor the copper salt may be reduced to the cuprous state by the addition of a sulphite, and the cuprous salt thus formed may be kept in solution by adding an alkali chloride to the liquor. The material is impregnated with the liquor, and the black developed by steaming, ageing, or in any other manner.

Osmium tetroxide appears to be a very efficient catalyst of oxidations with free oxygen. It is stated that when oxidizable liquids containing a trace of the tetroxide, about 0·05 gr. per 100 c.c., are heated to a temperature between 50° and 60° with oxygen in a steel bomb under a pressure of 10 atmospheres rapid oxidation is frequently effected. Anthracene, for example, is quickly converted by this method into anthraquinone.[1]

The Drying of Oils.

The so-called "drying" oils, *e. g.* linseed oil, which are important ingredients in paints and varnishes, undergo oxidation when exposed to the air. The absorption of oxygen by the oil results, in the first place, in the formation of intermediate compounds which themselves act as catalysts in promoting the conversion of the oil into more of the same substances; ultimately those compounds are changed into rather indefinite oxidation products. This process of drying or hardening of the oil is, however, very slow, and it is usual to add some substance which has a catalytic effect in accelerating the oxidation. The quantity of the catalyst necessary is in all cases very small.

Manganese dioxide and red lead are frequently employed as "driers," and many other metallic oxides have at least some degree of catalytic activity; cobalt compounds appear

[1] Hofmann, *Ber.*, 1912, **45**, 3329.

to be more effective than those of lead. Turpentine, which absorbs oxygen with the formation of an unstable oxidation product, possibly a peroxide, has also some effect, and the same is true of the metallic salts of certain unsaturated organic acids, such as manganous linoleate and lead oleate. In general the oxidation of drying oils is promoted by the presence of suitable metallic " soaps." According to Mackey and Ingle [1] a metal which can form more than one oxide acts as a " drier " or oxygen carrier when in an oil-soluble form, provided that salts of the lower oxide are more stable than salts of the higher, and, further, the more oxides a metal can form the greater its catalytic power. It was found, for instance, that " soaps " of cobalt, manganese, nickel, cerium, lead, chromium, iron, and uranium are more active " driers " than the corresponding compounds of bismuth, silver, zinc, thorium, mercury, and aluminium.

Catalytic Bleaching of Oils.

A number of experiments on the influence of catalysts on the velocity of the bleaching of palm oil by atmospheric oxygen are described by Hashmat Rai.[2]

The oil, mixed with small proportions of different catalysts, was heated in an autoclave by means of steam, and air from a compressor blown through. It was found that the addition of from 0·02 to 0·1 per cent. of a cobalt soap to the oil reduced the time of bleaching very considerably, whilst the product was of good quality. Manganese soaps and other metallic soaps possess similar properties, but the cobalt compound is the most active.

Electrolytic Oxidation.

Electrolytic oxidation, by oxygen liberated at the anode, is in many cases accelerated by the presence of catalysts.

A good example of this is the electrolytic method for the preparation of anthraquinone. Finely powdered anthracene

[1] *J. Soc. Chem. Ind.*, 1917, **36**, 317. [2] *Ibid.* 1917, **36**, 948.

is added to 20 per cent. sulphuric acid containing 2 per cent. of ceric sulphate as catalyst, in a leaden vessel which acts as the anode; a lead plate forms the cathode. The temperature is raised to from 70° to 100° during the operation, and the liquid is well agitated. Using an anodic current density of five ampères per sq. dcm. and 2·8–3·5 volts, the current efficiency is practically 100 per cent. The product is very pure, and the yield almost quantitative.[1]

Besides ceric sulphate chromic acid may be used; each oxidizes the anthracene readily and completely to anthraquinone, being reduced in the process to cerous sulphate and chromium sulphate respectively. By the anodic action of the current the original oxidizing salts are regenerated and the reaction proceeds. Both give a good product, but the action of ceric sulphate is much quicker than that of chromic acid. The anthracene may be directly added to the electrolyser in which the ceric sulphate is regenerated, and the oxidation of the hydrocarbon is so rapid that so long as any of it is present there is no possibility of cerous sulphate being formed by reduction at the cathode with consequent loss of current. With chromic acid, on the other hand, the spent liquors must be drawn off, electrolytically regenerated in a different vessel, and returned to the oxidizing vessel. Vanadic acid can be used with advantage instead of ceric sulphate, and in this case also the bath can be used over again after removal of the anthraquinone.

In a similar manner the preparation of benzoquinone from aniline can be carried out electrolytically, and naphthalene can also be oxidized with the acid of cerium salts, yielding according to the conditions of the operation either naphthaquinone or phthalic acid.

Oxidation with Sulphuric Acid.

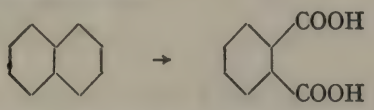
Concentrated sulphuric acid is, of course, capable of acting as an oxidizing agent, especially when heated to near its boiling point, and in many cases the velocity of the reaction is greatly increased by the addition to the acid of small

[1] Eng. P. 19178 (1902).

quantities of such catalysts as mercury or copper or their salts.

A familiar illustration is found in the Kjeldahl method of oxidizing organic nitrogen compounds, for the quantitative estimation of nitrogen, by means of hot concentrated sulphuric acid, containing small quantities of mercury or of copper or of the sulphates of those metals. The influence of the catalyst is very marked; thus it has been found that, at a temperature of 275°, the addition of 0·5 per cent. of mercuric sulphate to the sulphuric acid increases the velocity of oxidation of aniline threefold. Moreover, in this case, as in many others, the acceleration produced by the combined action of mercuric sulphate and cupric sulphate is greater than the sum of the accelerations brought about by each of these catalysts separately.

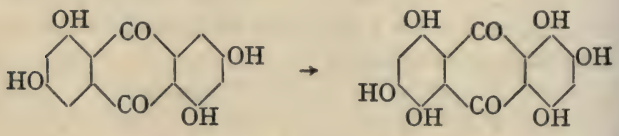
Another well-known example is the manufacture of phthalic acid from naphthalene, a process important because it is the first step in the preparation of synthetic indigo and of many other substances:—



When naphthalene is warmed with concentrated sulphuric acid, naphthalene sulphonic acids are formed, but at temperatures above 200° the acid acts as an oxidizing agent, phthalic acid and sulphophthalic acids being produced along with water and sulphur dioxide. The addition of mercury or of mercuric sulphate causes a remarkable increase in the speed of the process, especially as regards the fission of sulpho-groups from the sulphonic acids. It does not matter whether mercury itself or a mercury salt is used, since in either case the hot acid quickly produces mercuric sulphate. It is stated that, at 275°, the addition of 1 per cent. of mercuric sulphate to the acid causes the reaction to proceed with a velocity five times greater than that attained when the catalyst is absent. The use of oxides of cerium, of lanthanum, and of other rare earth metals has been proposed,

but apparently these catalysts do not possess the same advantages as mercury in this process.

The preparation of hydroxyanthraquinones through the action of sulphuric acid on anthraquinone or hydroxyanthraquinones is reported to be greatly accelerated by the addition of a mercury salt to the acid. It is an advantage to add also some boric acid, which protects the hydroxyl groups present in the compounds from further change by the formation of esters. For example, in order to obtain 1:2:4:5:6:8-hexahydroxyanthraquinone 10 kilos of 1:3:5:7-tetrahydroxyanthraquinone are heated with 200 kilos of sulphuric acid of 66° Bé., 5 kilos of crystallized boric acid, and 0·5 kilo of mercuric sulphate at a temperature between 200° and 250° until the reaction is complete. The hexahydroxy-compound is obtained in solid form by pouring the product into water.



Oxidation with Hydrogen Peroxide.

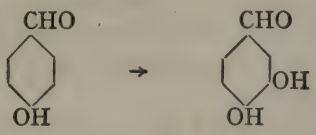
The method of oxidation with hydrogen peroxide in presence of small quantities of ferrous salts, which was introduced by Fenton,[1] is specially useful in the case of polyhydric alcohols and of hydroxy-acids, which in general are converted into the corresponding hydroxy-aldehydes (aldoses) and keto acids respectively. Thus, for instance, glycerol when treated with this oxidizing agent yields glyceric aldehyde ($CH_2OH{\cdot}CHOH{\cdot}CH_2OH \rightarrow CH_2OH{\cdot}CHOH{\cdot}CHO$), and malic acid is transformed into oxalacetic acid :—

$$COOH{\cdot}CHOH{\cdot}CH_2{\cdot}COOH \rightarrow COOH{\cdot}CO{\cdot}CH_2{\cdot}COOH.$$

The reaction takes place very readily, and with satisfactory yields, in the case of compounds containing the —CHOH·CHOH— group.

[1] *Chem. Soc. Trans.*, 1894, **65**, 899, and other papers.

Benzene itself and such derivatives as phenols and hydroxyaldehydes are also attacked by hydrogen peroxide with the aid of traces of ferrous salts. Benzene yields phenol and catechol, and *p*-hydroxybenzaldehyde is converted into protocatechuic aldehyde[1]:—



Oxidation with Nitrobenzene.

In a number of important manufacturing processes nitrobenzene is used as an oxidizing agent because of the comparative readiness with which it gives up oxygen, undergoing reduction to aniline, and some of these processes are carried out with the aid of iron or of ferrous salts which act catalytically as oxygen carriers.

In the manufacture of magenta, for instance, by Coupier's method, a mixture of 150 kilos of *o*-toluidine, 200 kilos of *o*-toluidine hydrochloride, 50 kilos of methyl sulphate (which yields methyl alcohol on heating), 150 kilos of nitrobenzene or of *o*-nitrotoluene, and 20 kilos of iron turnings is heated for 36–40 hours at 120°. After cooling the melt is broken up, the toluidine still present removed in a current of steam, the solution filtered, and the dye salted out.

The action of the catalyst is in this case easily understood. The ferrous salt formed by the action of the hydrochloric acid on the iron is oxidized by the nitrobenzene to ferric chloride; this oxidizes the toluidine, being reduced to ferrous chloride, and so the reaction proceeds.

Oxidation with Nitric Acid.

In various processes in which nitric acid is employed as an oxidizing agent, the reactions are accelerated by the addition of catalysts such as vanadic acid, mercury, mercuric nitrate, etc. For example, in the preparation of oxalic

[1] D. R. P. 155731.

acid from cane sugar the addition of less than 0·1 per cent. of ammonium vanadate or of vanadium pentoxide to the nitric acid promotes the action to such an extent that it proceeds without any external heating. A method of preparing oxalic acid by the action of nitric acid on solutions of carbohydrates in presence of a catalyst has been protected;[1] the oxides of nitrogen liberated in the process are oxidized to nitric peroxide, which is passed back into the reaction mixture.

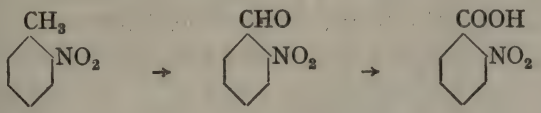
One of the methods of preparing anthraquinone consists in treating anthracene with nitric acid in presence of a mercury salt and an indifferent liquid at a temperature below 60°, and then converting the product thus obtained, which is a mixture of unstable mesonitro-derivatives of anthracene, into anthraquinone by treatment with an oxidizing agent in presence of a mercury salt at a temperature above 60°. For example, 117 parts of 80 per cent. anthracene are suspended in 300 parts of nitrobenzene, heated to 30°, and a solution of 3 parts of mercury in 460 parts of 31 per cent. nitric acid is added during three hours. The solution is filtered and heated for three hours more, and the nitric acid then separated (360 parts being recovered). The solution in nitrobenzene is treated with a solution of 5 parts of mercury in 55 parts of nitric acid (40° Bé.) and heated to 105° in the course of twenty-five minutes. The temperature rises rapidly, and as it falls, at about 110°, chlorine is passed in to remove organic compounds of mercury. After cooling the anthraquinone is filtered off, washed with nitrobenzene and then with benzene, and dried.[2]

Oxidation with Hypochlorites.

Cobalt salts, as is well known, accelerate the liberation of oxygen from solutions of bleaching powder very energetically, and the oxygen of hypochlorites is also rendered readily available through the catalytic action of the oxide or the chloride of nickel

[1] U.S. P. 1157348. [2] *Ibid.* 1119546.

When *o*-nitrotoluene is subjected to steam distillation in presence of these catalysts with slow addition of a solution of sodium hypochlorite, it is converted into *o*-nitrobenzaldehyde, which passes over with the steam, and *o*-nitrobenzoic acid, which remains in the distillation flask [1] :—



Oxidations with Alkali Chlorates.

Solutions of the alkali chlorates readily act as oxidizing agents in the presence of catalysts in many cases where in their absence the oxidizing action takes place very slowly or not at all. Among the catalysts which have been used to activate the chlorate solutions are compounds of vanadium, cerium, copper and iron, osmium tetroxide, and formic acid.

The valuable dye Aniline Black is made by oxidizing aniline hydrochloride in the cold with rather less than the calculated quantity of potassium or sodium chlorate, both in solution, in presence of oxygen carriers, such as a salt of vanadium or copper sulphate. Vanadium compounds are specially efficient, 1 part of the pentoxide being able to convert as much as 270,000 parts of aniline hydrochloride into the dye in presence of a sufficiency of the alkali chlorate. In point of efficiency vanadium compounds are followed by compounds of cerium and then of copper; iron compounds also act catalytically, but their action is much less vigorous; the effect of osmium tetroxide is said to be superior even to that of vanadium or cerium compounds in such processes as the oxidation of anthracene to anthraquinone, or of aniline to Aniline Black. In all these actions the catalysts are effective in conveying oxygen from the chlorate to the substance undergoing oxidation.

Hofmann and Schumpelt [2] state that in the oxidation of

[1] D. R. P. 127388.

[2] *Ber.*, 1915, **48**, 816.

certain compounds by solutions of chlorates in presence of osmium tetroxide, the liquid becomes acid and appreciable quantities of chlorine peroxide are produced. At this stage of the process the action increases in velocity, and it has been found that this effect is due to the formation of formic acid. If formic acid is added to a solution of a chlorate the latter is reduced to chlorine peroxide, which is formed more rapidly than it is removed, and so becomes free for other oxidation purposes. In this way substances which are not affected by a solution of a chlorate, *e. g.* indigotin, aniline, and anthracene, may be oxidized by a mixture of the chlorate with formic acid.

CHAPTER VI

Hydration and Hydrolysis

The reactions between water and organic compounds may be grouped broadly in one or other of two classes: firstly, *hydrations*, or the direct addition of the elements of water to unsaturated hydrocarbons, etc., or to such compounds as the anhydrides of organic acids, amides, lactones, etc., and, secondly, *hydrolyses*, that is to say, reactions in which the addition of the elements of water is accompanied by the breaking down of the molecule of the original substances into two or more molecules, as occurs when esters, glucosides, polysaccharides, etc., are hydrolysed.

Hydrations of all kinds are, as a rule, greatly facilitated by the addition to the water of small quantities of catalysts, amongst which mineral acids and strong bases are frequently very effective. When such catalysts are used in dilute aqueous solutions, their effect is attributed to the hydrogen or the hydroxyl ions produced by the electrolytic dissociation of the molecules of the acid or the base respectively.

The reversible reaction between an ester and water, which results in the formation of an acid and an alcohol—

$$R{\cdot}CO{\cdot}OR' + HOH \rightleftharpoons R{\cdot}CO{\cdot}OH + R'{\cdot}OH,$$

proceeds as a rule very slowly, and it may be a very long time before a state of equilibrium is attained in the system. If, however, even a very small quantity of a strong acid, for example, hydrochloric acid, is added the velocity of the reaction is greatly increased, and equilibrium may be reached in the course of an hour or two. The acid plays the part of a catalyst, and the catalytic effect of an acid is, within certain limits, proportional to the quantity added. With dilute solutions of different acids at the same molecular concentration the intensity of the catalytic action is

proportional to the relative strengths of the acids, or, in other words, to the concentration of hydrogen ions in the solution.

Soluble bases produce similar effects, but in this case the active catalysts are the hydroxyl ions : a very much smaller quantity of the base than can be neutralized by the liberated acid is effective in accelerating the hydrolysis of the ester, as is seen, for example, in the hydrolysis of fats with the aid of lime.

Preparation of Acetaldehyde from Acetylene.

The preparation of acetaldehyde from acetylene by hydration of the unsaturated hydrocarbon—

$$CH{:}CH + H_2O = CH_3{\cdot}CHO,$$

is carried out in general by passing a current of acetylene into an aqueous solution of an acid in presence of a mercury salt, which acts as a catalyst, and separating the aldehyde produced. The effect of the catalyst in this reaction can be attributed to the continuous formation of intermediate compounds by the action of the acetylene on the mercury salt and their subsequent decomposition by the aqueous acid. Numerous patents which cover the process differ mainly in their claims with respect to the nature and the concentration of the acid employed, the temperature at which the reaction is carried out, and the method of recovering the aldehyde; the following examples will serve to illustrate the various proposals.

Acetylene is passed into a solution of a mercury salt in at least 45 per cent. sulphuric acid, or at least 25 per cent. phosphoric acid, at temperatures below 70° and preferably at the ordinary temperature, when acetaldehyde and its condensation products and polymerides are obtained. The formation of further condensation products such as crotonic acid is greater the higher the concentration of the acid. The process can be stopped at intervals in order to separate the products by distillation or by precipitation with a neutral

salt such as sodium sulphate.[1] Another patent [2] claims the use of a liquid which readily dissolves acetaldehyde, but is insoluble in the solution of the mercury salt, and others [3] advocate the employment of a mercury salt dissolved in a highly concentrated organic acid, or a mineral acid other than sulphuric or hydrochloric acid, at temperatures below 50°; the aldehyde may be extracted from the resulting mixture by naphtha, etc., or the reaction may be carried out in presence of an immiscible solvent for the aldehyde.

It has also been proposed [4] that the acetylene should be introduced into a hot solution of the mercury salt, so that the aldehyde is distilled off as soon as it is formed, and again [5] that the reaction should be carried out at a temperature below the boiling point of acetaldehyde, but high enough for the aldehyde to be carried over by the excess of acetylene, from which it is removed by washing with water, the acetylene being passed into a second vessel.

The most favourable condition for the formation of acetaldehyde from acetylene, mercuric oxide, and sulphuric acid is said [6] to be attained if the sulphuric acid is employed in the dilute state and not concentrated as formerly recommended. The solution should not contain more than 60 gr. of sulphuric acid per litre, and the temperature should be kept well above the boiling point of the aldehyde, say, between 70° and 80°. In these conditions the yield is stated to be almost quantitative. On the other hand, a later patent [7] recommends the use of moderately concentrated acids, as in this way the rate of reduction of the mercury salts is diminished. This reducing effect appears to cause trouble, and a method has been patented [8] for impeding the separation of mercury by addition of small quantities of a ferric salt, for example, the sulphate, or of a compound of hexavalent chromium, *e. g.* chromic acid, to the solution.

Solutions or suspensions of sulphonic acids together with

[1] Eng. P. 29073 (1910).
[2] D. R. P. 250356.
[3] *Ibid.* 253707 and 253708.
[4] Fr. P. 460553.
[5] *Ibid.* 474246.
[6] *Ibid.* 455370.
[7] *Ibid.* 474246.
[8] U.S. P. 1151928 and 1151929.

a mercury compound, or of the mercury salts of sulphonic acids, are claimed [1] to have a power of hydrating acetylene considerably greater than that of solutions of mineral acids of the same acidity. For example, 21·6 parts of mercuric oxide are heated with 417 parts of *o*-chlorophenolsulphonic acid and 583 parts of water to a temperature of 30°–35°, and acetylene passed in; when absorption of the gas has diminished considerably, the aldehyde is removed by heating or by a current of steam; the yield of aldehyde is 300 parts.

According to another patent [2] the rapidity of the conversion of acetylene into acetaldehyde by combination with water in presence of a salt of mercury is greatly increased by carrying out the reaction in glacial acetic acid, at a temperature between 80° and 95°, adding water only as it is required. For example, acetylene is passed into a well-stirred mixture of 1000 gr. of glacial acetic acid, 22·5 gr. of sulphuric acid and 100 gr. of mercuric oxide at 80°–85°. The excess of acetylene passes through a fractionating apparatus, a condenser cooled by a freezing mixture, an absorption vessel charged with water (in which the aldehyde is absorbed), and then back to the reaction vessel. The acetylene is absorbed at the rate of from 100 to 200 litres per hour. Water is added to the reaction vessel at the same rate as it is used up in the reaction. The reaction vessel may be of iron, nickel, or other metal not attacked by concentrated acetic acid. Mercury salts of other strong acids may be used.

One other process may be mentioned, since it differs entirely in character from those already referred to. This [3] consists in passing a mixture of acetylene with steam, in the proportion of 1 : 4 by volume, over bog iron ore heated to 400°–420°. The gases from the reaction vessel are cooled, and the portion which does not condense is washed with water, glacial acetic acid or other absorbents. Acetaldehyde is obtained as chief product of the reaction, together with small quantities of other products of condensation such as

[1] Fr. P. 469497. [2] Eng. P. 5132 (1915).
[3] *Ibid.* 109983 (1916).

acetone, higher aldehydes, etc., and part of the aldehyde is oxidized to acetic acid. If the mixed gases are passed only once over the heated catalyst, about 15 per cent. of the acetylene is converted into acetaldehyde; with mixtures containing smaller proportions of steam larger quantities of the higher condensation products are formed.

According to a later patent [1] a mixture of purified acetylene and steam is passed at a high temperature over a catalyst consisting of oxides or combinations of oxides. The exhausted catalyst, *e.g.* molybdic acid, is regenerated and freed from catalyst poisons by treatment at a high temperature with a current of air.

Preparation of Acetic Acid from Acetylene.

The direct conversion of acetylene into acetic acid by simultaneous hydration and oxidation—

$$CH{:}CH + H_2O + O = CH_3{\cdot}CO{\cdot}OH,$$

can be effected in various ways, acetaldehyde, of course, being formed as an intermediate product and oxidized as produced without being isolated. For instance, acetylene is passed through solutions of hydrogen peroxide or of persulphuric acid in presence of mercury compounds,[2] or else is oxidized electrolytically, using as electrolyte dilute sulphuric acid containing a mercury compound.[3]

Acetic acid is readily synthesized by the interaction of acetylene, oxygen, and the requisite amount of water in presence of salts of mercury such as the acetate, sulphate, or phosphate. The reaction is carried out in acetic acid or in any appropriate organic acid, *e.g.* chloroacetic or lactic acid, which can be readily separated from the acetic acid formed. Contact substances such as iron oxides or vanadium pentoxide and accelerating agents such as phosphoric or sulphuric acid or bisulphates may be used in addition to the mercury salts. The best results are obtained by introducing acetylene

[1] U.S. P. 1244901, 1244902. [2] Fr. P. 467515.
[3] *Ibid.* 467778.

and oxygen alternately into the acid mixture containing the contact substance.[1]

According to another process [2] a liquid medium is employed in which the mercury salt is in solution, *e.g.* acetic acid, or which has a greater solvent power for acetylene than water, as, for example, acetone. Oxidizing substances such as hydrogen peroxide, perborates, percarbonates, permanganates, dichromates, ozone, etc., are added, or the oxidation may be effected by oxygen or air with or without catalysts such as cerium oxide, vanadium pentoxide, copper acetate, platinum or palladium sponge, etc. As an example, into a mixture of 400 parts of glacial acetic acid, 100 parts of water, 50 parts of mercuric nitrate, and 10 parts of cerium oxide, are passed 130 parts of acetylene and from 80 to 100 parts of oxygen. Acetic acid is produced continuously and may be drawn off at intervals and distilled, the residue being returned to the reaction vessel.

Hydrolysis of Fats.

Hard fats are essentially mixtures of the glyceryl esters (glycerides) of stearic and palmitic acids. When heated with solutions of the caustic alkalis they are hydrolysed with formation of glycerol and the alkali salts of the fatty acids (soaps), but when water alone is used the hydrolysis results in the production of glycerol and the free fatty acids :

$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O = C_3H_5(OH)_3 + 3C_{17}H_{35}\cdot COOH.$$

The process of hydrolysis with water is slow and can only be effected at high temperatures, but if small quantities of catalysts such as lime are added the reaction can be carried out with much greater velocity and at a lower temperature.

The quantity of lime required for the conversion of a glyceride of molecular weight 890 into glycerol and the calcium salt of the fatty acid is 9·4 per cent. of the weight of the glyceride, but if the process is carried out at the ordinary pressure the hydrolysis cannot be completed unless the proportion of lime is increased to 12–14 per cent. If, however,

[1] Fr. P.473158. [2] *Ibid.* 479656.

the hydrolysis is effected under increased pressure it is possible to use the lime as a catalyst, strictly speaking. Thus at a pressure of 12 atmospheres (corresponding to a temperature of 190°) even 1 per cent. of lime suffices for complete hydrolysis of the fat, and at 8 atmospheres with about 3 per cent. of lime the fat is practically completely hydrolysed after from 8 to 10 hours. Hence in practice the process is carried out in an autoclave; when it is completed the free fatty acids, containing as much lime soap as corresponds to the quantity of lime introduced, rise to the surface and are easily separated from the aqueous solution of glycerol.

In this process of hydrolysis the base can be replaced by an acid, and concentrated sulphuric acid has been used with satisfactory results. The fat, previously heated to 120° or more in order to remove the last traces of moisture, is rapidly mixed with from 4 to 6 per cent. of its weight of sulphuric acid of 66°–67° Bé.; various mixing machines are used to ensure the most intimate contact of the acid with the fat within the shortest possible time in order to reduce to a minimum secondary reactions and destruction of the fatty matter. The sulphonated mass is run into boiling water and agitated by means of steam until the sulphonic acids are hydrolysed; on standing separation occurs into a lower aqueous layer containing glycerol and the sulphuric acid and an upper layer of fatty acids.

A valuable modification of the process of hydrolysing fats is that devised by Twitchell,[1] in which the fat is agitated with water in presence of a relatively small proportion of a salt of a sulpho-aromatic fatty acid and of a suitable quantity of an acid capable of combining with the metal so that the sulpho-acid is liberated. The charge is heated and agitated until the fatty acids and glycerol separate, after which the metal of the salt is precipitated and the products of hydrolysis are collected.

The fat is hydrolysed in loosely covered wooden tanks by digestion with water and as little as 0·5 per cent. of the catalyst, and at a temperature not exceeding that of

[1] Fr. P. 456956.

exhaust steam. Hence the use of autoclaves is done away with, and the reaction may be carried out on a scale limited only by the size of the tank. The catalysts first employed were sulphonic derivatives of the fatty acids, such as sulpho-stearic and sulpho-oleic acids, but further experience showed that a better catalyst was produced by introduction of an aromatic radicle into the compound, and at present such compounds as sulphophenylstearic acid, $SO_3H \cdot C_6H_4 \cdot C_{18}H_{35}O_2$, and sulphonaphthylstearic acid, $SO_3H \cdot C_{10}H_6 \cdot C_{18}H_{35}O_2$, are employed. These substances have the property of dissolving both in fat and in water, and of rendering them mutually soluble. The salts of such metals as barium, calcium, magnesium, aluminium, etc., can be obtained as stable dry powders, and these can be used with addition of the quantities of hydrochloric or sulphuric acid necessary to liberate the sulpho-acid.

A process such as this is suitable for the production of crude glycerol free from salts, whilst the free fatty acids can be converted directly into soaps by treatment with sodium carbonate.

Other examples of hydrolysis effected with the aid of acids as catalysts are the inversion of cane sugar, and the manufacture of glucose from starch, which are so well known that description of the processes is unnecessary.

Dehydration

An immense number of reactions in which carbon compounds containing hydroxyl groups take part result in the formation of water as one of the products. These processes of dehydration fall into two groups: firstly, those in which the ultimate result is the simple elimination of the elements of water from a compound, as for instance the formation of ethylene from ethyl alcohol; and, secondly, those in which the formation of water takes place at the expense of two or more molecules of carbon compounds, which at the same time become linked together, for example, the production of one molecule of diethyl ether from two of ethyl alcohol,

or of one molecule of an ester by the interaction of one molecule of an acid and one of an alcohol. Some examples of each class follow.

Dehydration of Alcohols.

The dehydration of primary alcohols results, according to the conditions, in the formation of an ether or of an unsaturated hydrocarbon. Thus from ethyl alcohol either diethyl ether or ethylene can be obtained :—

(1) $CH_3 \cdot CH_2 \cdot OH + HO \cdot CH_2 \cdot CH_3 = H_2O + CH_3 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_3$;

(2) $CH_3 \cdot CH_2OH = H_2O + CH_2 : CH_2$.

Secondary alcohols as a rule and tertiary alcohols always yield only unsaturated hydrocarbons.

Such reactions are brought about by a number of different dehydrating agents, of which concentrated sulphuric acid, phosphoric acid, or anhydrous zinc chloride are most commonly used; for instance, when ethyl alcohol is heated with concentrated sulphuric acid at 140° the formation of ether takes place, whilst at higher temperatures, about 160°–170°, ethylene is the chief product.

In carrying out this process for the preparation of ethylene it is usual to add to the mixture of alcohol and sulphuric acid a small quantity of sand in order to prevent " bumping." Senderens [1] has found that the sand also acts catalytically in accelerating the reaction, and that anhydrous aluminium sulphate is a more powerful catalyst. With the usual mixture of one volume of 95 per cent. alcohol and two volumes of concentrated sulphuric acid, at a temperature of 157°, the volume of ethylene produced per minute was found to be, with no catalyst, 12 c.c.; with addition of sand, 50 c.c.; and with addition of 10 gr. of anhydrous aluminium sulphate per 200 c.c. of liquid, 160 c.c.

A similar catalytic effect influences the production of ether. With a mixture of four volumes of 95 per cent.

[1] *Compt. rend.*, 1910, **151**, 392.

alcohol and three volumes of concentrated sulphuric acid, production of ether begins at 140°, but if the aluminium salt is added to the mixture in the proportion of 5 gr. per 100 c.c. ether begins to be formed at 110°, and distils regularly at 120° and rapidly at 130°. Above 140° ethylene passes over with the ether, increasing in quantity as the temperature is raised. With higher, *e.g.* propyl and isobutyl, alcohols the chief reaction is the production of the corresponding olefine, and the formation of these is also accelerated by the addition of aluminium sulphate.

The dehydration of alcohols can also be effected by passing their vapours over heated catalysts. Under these conditions the normal reaction is the formation of an unsaturated hydrocarbon and not of an ether, because the latter substances themselves readily undergo dehydration at the high temperatures, usually 300° or above, at which the process is carried on. The most effective catalysts were found by Sabatier and Mailhe to be alumina, thoria, the blue oxide of tungsten (W_2O_5), and kaolin; especially in the case of alumina, the physical state has much influence on the activity of the catalyst, for as the action is a surface one the amorphous oxides prepared from the precipitated hydroxides at as low a temperature as possible are much more active than the oxides in a crystalline state or after ignition at a red heat. Alumina prepared at a temperature below 400° is a very active catalyst towards the alcohols, but when calcined at a bright red heat has almost no catalytic power. Thoria, on the contrary, may be heated to redness without marked loss of activity. The activity of the oxides always diminishes with use, because by degrees a deposit of tarry or carbonaceous matter is formed on the surface, and no doubt because in addition the oxide tends to pass into the crystalline state. Thoria which has lost its activity may be regenerated by exposure to a red heat for a few minutes. With any of these catalysts increase of temperature greatly increases the velocity of the reaction, but, on the other hand, tends to render more prominent the dehydrogenation of the alcohol, and the consequent formation of an aldehyde and

hydrogen. Increase of pressure has the effect of retarding the dehydration.

This method of dehydration of alcohols has been applied in several cases, among which the following may be quoted.

Preparation of Ethylene by the action of Heated Alumina on the Vapour of Ethyl Alcohol.[1]

In the preparation of ethylene from ethyl alcohol the catalytic action of the alumina is dependent not only on the temperature but also on the physical state of the catalyst, the amorphous oxide alone giving a good yield. The value of a sample can be tested to some extent by shaking it with water; active specimens form a suspension whilst the particles of inactive specimens settle quickly. Care must be taken to maintain the temperature at the point at which the yield of ethylene is greatest, namely, 360°. If the temperature is above this point the ethylene begins to decompose, the yield of gas diminishes because the amorphous oxide of aluminium is slowly converted into the crystalline form, and moreover the nature of the action of the catalyst on the oxide may be altered in such a way that acetaldehyde and hydrogen are found among the products. On the other hand, if the temperature is below 360° not only does the yield of ethylene diminish, but a considerable amount of ether may pass into the ethylene.

The primary decomposition of ethyl alcohol in presence of alumina, which takes place at about 230°, results in the formation of ether and water :—

$$2CH_3{\cdot}CH_2OH = CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3 + H_2O.$$

At 360° the ether itself undergoes decomposition into ethylene and water :—

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3 = 2CH_2{:}CH_2 + H_2O.$$

Hence, unless the temperature of the whole apparatus containing the catalyst is maintained at 360° a portion of

[1] Sprent, *J. Soc. Chem. Ind.*, 1913, **32**, 171; Ipatiev, *J. Soc. Chem. Ind.*, 1913, **32**, 638.

the ether may pass through undecomposed, especially in an apparatus on a large scale. In such a case the ethylene always contains some ether, sometimes as much as 10 per cent. The formation of ether can be reduced to a small percentage by preheating the alcohol vapour to 360° before it is passed through the tubes containing the catalyst. For the production of ethylene in quantity iron tubes 1·5 metres in length and 7·5 cm. in diameter were used; these were connected with the vessel in which the alcohol was heated.

Ethylene prepared in this way is not sufficiently pure for the catalytic synthesis of ethane, because it contains impurities which gradually poison the nickel and eventually make it entirely inactive. Traces of impurities such as ether, acetaldehyde and isoprene can be condensed by compressing the ethylene at about 50 atmospheres pressure and removed by a suitable contrivance in the apparatus. If the alumina contains any sulphates traces of sulphuretted hydrogen may be found in the gas, but this may be removed by a solution of lead acetate. Finally, washing of the gas with concentrated sulphuric acid is essential in order to remove certain unidentified impurities which also act as poisons to nickel.

Other examples of the preparation of unsaturated hydrocarbons by the dehydration of various compounds are found in several patented processes for the production of isoprene, etc. According to one of these, isoprene is obtained by passing the vapours of "an isoamylene oxide," or of a methylbutane diol, *e.g.* 1:3-dihydroxy-2-methylbutane, or of methyl isobutyl ketone over a dehydrating catalyst such as aluminium silicate at less than atmospheric pressure and at temperatures between 400° and 600°. For example, the diol referred to breaks down thus :—

$$CH_2OH{\cdot}CH(CH_3){\cdot}CHOH{\cdot}CH_3 = 2H_2O + CH_2{:}C(CH_3){\cdot}CH{:}CH_2.$$[1]

Analogous to this is the preparation of isoprene by heating methylbutenol esters with a catalytic substance which will

[1] U.S. P. 1094222, 1094223, 1106290.

eliminate the acid of the ester, for example, alumina, barium chloride, or nickel chloride, at high temperatures and preferably under reduced pressure; a good yield is obtained when alumina is used as the catalyst at 400° and 50 mm. pressure. Thus methylbutenol acetate yields acetic acid and isoprene :

$$CH_3{\cdot}C(CH_3)(OCOCH_3){\cdot}CH{:}CH_2 = CH_3{\cdot}COOH + CH_2{:}C(CH_3){\cdot}CH{:}CH_2.$$ [1]

According to Ostromisslenski,[2] in presence of catalytic dehydrating agents such as red phosphorus, sulphanilic acid, barium chloride, and especially alumina, acetaldehyde or para-acetaldehyde condenses with ethyl or with propyl or isopropyl alcohol, yielding erythrene or piperylene respectively :—

(1) $CH_3{\cdot}CHO + CH_3{\cdot}CH_2OH = 2H_2O + CH_2{:}CH{\cdot}CH{:}CH_2$;

(2) $CH_3{\cdot}CHO + (CH_3)_2CHOH = 2H_2O + CH(CH_3){:}CH{\cdot}CH{:}CH_2$.

Precipitated alumina gives the best results, but its action is due partly to the presence of various impurities such as basic aluminium salts; as the reaction proceeds throughout the mass the alumina must be sufficiently porous and hygroscopic. The catalyst soon exhibits fatigue, which is due to the deposition on it of resinous and carbonaceous products, but may be regenerated by exposure to a red heat and subsequent treatment with water at the ordinary temperature. The best temperature for the reaction is from 360° to 400°; the mixed vapours of aldehyde and alcohol should be heated rapidly to this temperature, and the products of the reaction quickly removed from the region of high temperature. The reaction is promoted by reduction of the pressure. It is stated that mixtures containing 1, 1·5, or 2 parts of alcohol to 1 part of aldehyde give approximately identical yields of erythrene, which may amount to 25 per cent. of the crude or 16 to 18 per cent. of the pure hydrocarbon.

[1] Eng. P. 13327 (1913).

[2] *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1494, 1507.

Dehydration of Organic Acids.

A catalytic method for the preparation of anhydrides from the corresponding carboxylic acids depends upon the use of acetylene as a dehydrating agent in presence of a catalyst such as a mercury salt, a small quantity of an oxidizing agent, for example, potassium dichromate, being added at the beginning of the reaction. When acetic acid is treated by this method, acetic anhydride and ethylidene diacetate are produced :—

(1) $CH{:}CH + 2HO{\cdot}CO{\cdot}CH_3 = CH_3{\cdot}CHO + (CH_3CO)_2O$;
(2) $CH_3{\cdot}CHO + (CH_3CO)_2O = CH_3{\cdot}CH(OCOCH_3)_2$.

Since the ethylidene diacetate breaks down on heating ($CH_3{\cdot}CH(OCOCH_3)_2 = CH_3{\cdot}CHO + (CH_3CO)_2O$), the mixture can be separated by fractional distillation into acetic anhydride and acetaldehyde, or otherwise can be used as a solvent for cellulose acetate or other cellulose compounds.[1]

In processes such as the above, if the catalyst is formed in contact with the substance which is to react with the acetylene the reaction takes place more quickly and completely, and with less tendency towards the formation of tarry matters. For instance, in the production of ethylidene diacetate from acetylene and acetic acid the catalyst, mercuric sulphate, instead of being added as such is formed by first dissolving mercuric oxide in the acetic acid and then adding the quantity of sulphuric acid necessary to convert it into the sulphate.[2]

Preparation of Nitriles.

A familiar method of preparing nitriles is the distillation of the amides or the ammonium salts of organic acids with phosphorus pentoxide : $R{\cdot}CONH_2 = RCN + H_2O$. The reaction may also be effected catalytically by passing a mixture of the vapour of an organic acid and ammonia over heated alumina or thoria : $RCOOH + NH_3 = RCN + 2H_2O$.[3] For example, when the vapour of acetic acid mixed with a

[1] Fr. P. 474828. [2] *Ibid.* 475853.
[3] Epps and Reid, *J. Am. Chem. Soc.*, 1916, **38**, 2128.

slight excess of ammonia is passed through a tube filled with fragments of pumice upon which alumina has been deposited and maintained at a temperature of 500°, acetonitrile is formed, with a yield which may amount to 85 per cent. of the theoretical. The acetic acid, preferably anhydrous, and the ammonia are conveyed to the catalysing tube through separate inlets in such a way that the acid vapour enters directly into an atmosphere of ammonia at the reaction temperature. The condensed liquid in the receiver generally forms two layers, of which the upper contains the nitrile and the lower ammonium acetate. In time the catalyst becomes inactive, being coated over with a black deposit; its activity depends largely upon the method of preparation.

Preparation of Esters.

The direct formation of esters of organic acids by the interaction of an acid and an alcohol,

$$R{\cdot}OH + R'{\cdot}COOH = H_2O + R'{\cdot}COOR,$$

takes place slowly even when the mixture is heated, but is greatly accelerated by the presence of catalysts such as hydrochloric or sulphuric acid. Moreover, it has been proved[1] that only small quantities of the catalyst are necessary; thus when 2 parts of ethyl alcohol containing 3 per cent. of hydrochloric acid are heated with 1 part of benzoic acid the yield of ethyl benzoate amounts to about 67·5 per cent. of the theoretical quantity, and again when a mixture of 2 parts of the alcohol, 1 part of the acid, and 0·2 part of sulphuric acid is heated for some time a 90 per cent. yield of ester is obtained.

This method of making esters, many of which are employed for flavouring purposes and in making perfumes, is in general use, and is so well known as to make further description superfluous. This is also the case with modifications of the process such as the use of anhydrides or acid chlorides in place of the organic acids, but a recent proposal may be

[1] Fischer and Speier, *Ber.*, 1895, **28**, 3252.

noted. If a mixture of an ester of ethylidene glycol and an alcohol is heated, preferably in the presence of a small quantity of a catalyst such as sulphuric acid, acetaldehyde is evolved and the corresponding ester is contained in the residue; for example:—

$$CH_3{\cdot}CH(OCOCH_3)_2 + 2C_2H_5OH = CH_3CHO + H_2O + 2CH_3{\cdot}COOC_2H_5.$$

The reaction is said to be general, taking place with both primary, secondary, and tertiary alcohols, and with aromatic hydroxy-compounds.[1]

Sabatier and Mailhe have found that esters can also be prepared catalytically, and in some cases with very advantageous results, by passing mixtures of the vapours of an acid and an alcohol over heated thoria or titanium dioxide. The latter catalyst is preferable in most cases, because it is active at lower temperatures than thoria, and also because it retains its activity almost indefinitely. Thus when the vapours of benzoic acid and an alcohol are passed over thoria heated to 350°, the acid is largely converted into an ester; titanic oxide can be used at a temperature between 280° and 300°, and if the mixture contains at least 10 molecules of alcohol to 1 molecule of acid the latter is almost completely converted into an ester. In presence of these catalysts the reaction takes place at temperatures even as low as 120°–150°, but, of course, with lower velocity; at such temperatures even formic acid can be esterified in this manner. It is stated also [2] that when compounds of glucinum are used as catalysts the yields of ester are better than with thoria or titanic oxide.

Preparation of Acetals.

Acetals may be very conveniently used for many purposes in place of the aldehydes from which they are derived. The preparation of these compounds by the interaction of an aldehyde and an alcohol,

$$R{\cdot}CHO + 2HO{\cdot}R' = H_2O + R{\cdot}CH(OR')_2,$$

[1] Fr. P. 478435. [2] D. R. P. 261878.

is best carried out with the aid of catalysts, dilute alcoholic hydrochloric acid being in many cases the best. The reaction is also brought about, or at least promoted, by the action of other substances.

Acetals of the type $CH_3 \cdot CH(OR)_2$, in which R is an alkyl radicle, are obtained by treating a mixture of acetaldehyde and an aliphatic alcohol containing from 20 to 50 per cent. of the aldehyde, with hydrated or dehydrated chlorides or nitrates of aluminium, glucinum, calcium, cerium, lithium, magnesium, thorium, etc., with or without addition of hydrochloric or other acid. For example, 20 c.c. of a saturated solution of sodium chloride and 10 gr. of sodium chloride are added to 50 c.c. of a mixture containing 40 per cent. of acetaldehyde and 60 per cent. of ethyl alcohol together with 1 c.c. of concentrated hydrochloric acid, and the mixture shaken for some time; the upper layer is washed with water and then with sodium carbonate solution, dried over calcium chloride and then over potassium carbonate, and finally fractionated.[1]

In practice, the preparation is conveniently carried out as follows. To a mixture of acetaldehyde and ethyl alcohol containing about 33 per cent. of the former are added about one-tenth of its weight of anhydrous calcium chloride and a small quantity of hydrochloric acid. The mixture is shaken at intervals for about an hour, and then the upper layer which separates is poured into a vessel containing a fresh quantity of calcium chloride. After about half an hour, when a small lower layer of liquid usually separates, the treatment with calcium chloride is repeated for a third and then for a fourth time. The liquid is left to stand in contact with the last lot of calcium chloride for about twelve hours, then well shaken with anhydrous potassium or sodium carbonate to remove traces of acid, filtered, and fractionally distilled. Para-aldehyde may be utilized for the preparation by mixing it with three times its volume of alcohol, adding calcium chloride and hydrochloric acid, and then warming

[1] Eng. P. 101428 (1917).

on the water-bath for a few minutes; the rest of the preparation is as described.

Preparation of Mixed Ethers.

As has been already stated, the catalytic production of ethers from aliphatic alcohols at high temperatures is only possible in a few cases, for instance, in that of diethyl ether, which is obtained together with only a small quantity of ethylene when the vapour of ethyl alcohol is passed over alumina (prepared by precipitation and dried at a low temperature) heated to 240°.

Sabatier and Mailhe have found that better results are obtained in preparing aromatic ethers by this method, using thoria as the catalyst; thus when the vapour of phenol is passed over thoria heated to 400°–450° the condensed product contains about 50 per cent. of diphenyl ether, along with unaltered phenol and a certain proportion of diphenylene oxide. It is, however, in the preparation of mixed ethers, containing an aromatic and an aliphatic radicle, that the process is used with most advantage. The vapour of a phenol mixed with excess of the vapour of an aliphatic alcohol is passed through a tube containing thoria and maintained at a temperature between 390° and 420°; the excess of the alcohol is separated from the condensed product by fractional distillation. Particularly good results have been obtained with methyl alcohol and phenol, the cresols, thymol, carvacrol, and the naphthols, with production of phenyl methyl ether, etc.

Preparation of Amines.

Amines may be prepared by the interaction of alcohols and ammonia in presence of a catalyst, thoria being apparently the most effective: $R{\cdot}OH + NH_3 = R{\cdot}NH_2 + H_2O$. A mixture of the vapour of the alcohol and ammonia is passed through a tube containing thoria and maintained at a temperature varying from 250° to 350° according to the nature of the alcohol. The product obtained by condensa-

tion of the issuing vapours is a mixture of aqueous ammonia, the primary and secondary amines corresponding to the alcohol, and some unaltered alcohol containing a small quantity of an unsaturated hydrocarbon in solution; a trace of the tertiary amine is usually formed. In this way amines can be obtained readily from the lower fatty alcohols, benzyl alcohol, and cyclohexanol and its homologues.

Preparation of Thioalcohols.

Replacing ammonia in the above reaction with sulphuretted hydrogen, and using thoria as the catalyst at temperatures between 300° and 380°, yields of thioalcohols which surpass 75 per cent. of the theoretical quantities may be obtained: $R{\cdot}OH + H_2S = R{\cdot}SH + H_2O$. The other products are water and small quantities of alkyl sulphides and unaltered alcohol.

Polymerization

The polymerization of various classes of substances, that is to say, the union of two or more molecules of the substance with formation of a more complex molecule, is frequently either induced or accelerated by the action of catalysts.

Reference has already been made to the fact that the formation of benzene by the polymerization of acetylene, which in the absence of catalysts takes place at a low red heat, begins at much lower temperatures if the gas is in contact with finely divided nickel, iron, or other metals or substances of catalytic activity. It is possible that this observation will find practical application, for instance, in the production of benzene and other aromatic hydrocarbons from petroleum, or even from acetylene itself, but many factors will contribute to settle this point. On the other hand, a process which promises to be of great technical importance is the synthesis of rubber, or of substances closely similar in properties to natural rubber, by the polymerization of various unsaturated hydrocarbons.

Synthetic Rubber.[1]

Synthetic rubbers have been prepared by the polymerization of certain unsaturated hydrocarbons, particularly butadiene (erythrene), $CH_2{:}CH{\cdot}CH{:}CH_2$, and its homologues isoprene, $CH_2{:}C(CH_3){\cdot}CH{:}CH_2$, piperylene,

$$(CH_3)CH{:}CH{\cdot}CH{:}CH_2,$$

and dipropylene, $CH_2{:}C(CH_3){\cdot}C(CH_3){:}CH_2$. The polymerization may take place spontaneously, at the ordinary temperature or on heating, but the process is greatly accelerated by the presence of catalysts of various kinds. The rubbers so obtained, or some of them, are capable of being vulcanized just like natural rubber, the conditions under which they are formed are well defined, and it depends upon the cost of production whether or not they will be manufactured on the large scale.

In 1860 Greville Williams isolated isoprene in a fairly pure state from the products of the destructive distillation of rubber, and observed that the hydrocarbon becomes viscid when kept. If this "ozonized" isoprene is distilled, unaltered isoprene comes off first, the fluid thickens, the boiling point rises rapidly, and then a sudden reaction occurs, a cloudy vapour rising and the contents of the flask solidifying to a white, spongy mass which undoubtedly contains rubber.

In 1879 Bouchardat, in order to prepare the hydrochloride, shook up isoprene with a saturated solution of hydrochloric acid. On attempting to distil the hydrochloride produced he found that a proportion remained as a solid residue, which possessed the elasticity and other properties of rubber itself. Two years later Hofmann observed that piperylene, an isomeride of isoprene, also shows a tendency to polymerize during distillation.

In 1882 Tilden drew attention to the conversion of isoprene "into true india-rubber or caoutchouc when brought into

[1] Cf. Perkin, *J. Soc. Chem. Ind.*, 1912, **31**, 616; Potts, *J. Soc. Chem. Ind.*, 1913, **32**, 564.

contact with certain chemical reagents, *e. g.* strong aqueous hydrochloric acid as noticed by Bouchardat, or nitrosyl chloride as observed by myself," and pointed out that if it were possible to obtain isoprene from some other and more accessible source, the synthetical production of india-rubber could be accomplished. In 1892 Couturier found that dipropylene also polymerizes very easily, for instance, by the action of heat, and in the same year Tilden showed, for the first time, that synthetic rubber, which he had obtained by the spontaneous polymerization of isoprene, is capable of vulcanization, and therefore sufficiently resembles natural rubber to be used commercially.

In July 1910, Matthews sealed up some isoprene along with metallic sodium, and in the following month discovered that the contents of the tube had become viscid and contained a proportion of a remarkably good variety of rubber; a few weeks later the tube was found to contain a solid mass of amber-coloured rubber. Further work showed that sodium was a general polymerizing agent of the first importance for butadiene and its homologues, and a patent was applied for in October of that year. According to this patent,[1] to bring about the polymerization of divinyl (butadiene), isoprene, or homologues or derivatives thereof, these hydrocarbons are brought into contact with an alkali metal, or an alkaline earth metal, or an alloy or mixture or amalgam of any of such metals, in the presence or absence of any other metal or alloy. Metallic sodium or potassium is specially suited to this purpose. For example, 20 parts by weight of isoprene are brought into contact with 1 part by weight of sodium; a small part of the sodium goes into solution and after standing some time the liquid thickens, and on further standing at the ordinary temperature it becomes solid. The unpolymerized portions are removed, for example, by steam distillation or extraction with acetone. When potassium is used it is advisable to have present also some other metal to moderate its action. Products obtained from some of the higher homologues and derivatives

[1] Eng. P. 24790 (1910).

of isoprene are harder than and do not possess all the characteristics of actual caoutchouc.

This discovery of the value of sodium as a catalyst for promoting the polymerization of isoprene was made a month or two later, quite independently, by Harries.[1]

The action of sodium on isoprene and similar hydrocarbons is practically quantitative, and is not seriously affected by the presence of other hydrocarbons which cannot be polymerized to rubber. It may also be carried out in the cold, or with the application of very moderate heat. These advantages, it is claimed, do not belong to other polymerization processes which have been proposed.

Since the date of Matthews' patent many others have been taken out, relating either to new or modified methods of inducing the polymerization of suitable hydrocarbons such as isoprene, or to methods of obtaining such hydrocarbons. Some of the latter group are mentioned in other sections of the book, being classified according to the nature of the reactions involved; of the former group the following is a summary.

The polymerization of butadiene or its homologues with production of rubbers can be effected with the aid of anhydrides of organic acids as catalysts; for example, isoprene heated at 150° with acetic anhydride gives a product possessing the properties of caoutchouc.[2]

The hydrocarbons are heated with organic or inorganic acids, or with compounds having an acid reaction, or with sulphur, in proportions so small that they promote the process of polymerization without injuring the properties of the products. Thus an addition of 0·2 per cent. of sulphur or of 0·002 per cent. of sulphuric acid to the isoprene will greatly increase the yield of crude rubber.[3]

Bodies capable of yielding oxygen or of acting as oxygen carriers may be used as catalysts; for example, sodium in presence of air, old oxidized rubber, perborates, isoprene partially oxidized, etc.[4]

[1] *Ann.*, 1911, **383**, 157.
[2] Fr. P. 433825.
[3] *Ibid.* 434587.
[4] *Ibid.* 440173.

Butadiene or its homologues or analogous compounds, or mixtures of these, are submitted to the action of organo-metallic compounds, in particular the alkyl derivatives of the alkali or alkaline earth metals, or of magnesium; for example, the crystalline compound of sodium ethyl and zinc ethyl, or a mixture of 1 part of sodium wire and 3 parts of zinc ethyl.[1]

The polymerization of butadiene or its homologues or analogues to caoutchouc-like substances is considerably accelerated by the presence of colloidal metals,[2] or, when sodium is used as the catalyst, by carrying out the operation in an atmosphere of carbon dioxide.[3]

Isoprene is polymerized by heating with trioxymethylene, preferably in a closed vessel under pressure; both substances may be in a liquid form, or may be allowed to interact when in the state of vapour.[4]

Isoprene yields β-myrcene when left to stand alone, or in contact with a catalyst, *e. g.* barium peroxide, benzoyl peroxide, potassium sulphite, etc., or when heated to a temperature not exceeding 150°, and β-myrcene in turn polymerizes spontaneously, or by the action of heat, light, or electricity, either with or without a catalyst. For example, isoprene is heated for ten days at 80°–90° in a closed vessel, and the mixture of products thus obtained is heated with 20 per cent. of sodium wire at 70°.[5]

The hydrocarbon β-myrcene, mentioned in the patent last quoted, is described by Ostromisslenski [6] as a colourless mobile liquid, with a boiling point of 63°–63·5° at 20 mm. pressure. Its probable formula is :—

$$CH_2{:}CH{\cdot}C(CH_3){:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3){:}CH_2.$$

When heated at 60°–70° with sodium and barium peroxide it is quantitatively converted into "normal" caoutchouc, whereas under similar conditions isoprene would yield an "abnormal" caoutchouc. It can also be polymerized by

[1] Fr. P. 446600.
[2] D. R. P. 264959.
[3] Fr. P. 459005.
[4] *Ibid.* 459987.
[5] *Ibid.* 475565.
[6] *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1941.

heating at 70° with sodium alone (5 per cent.), or by being left to stand for some months at the ordinary temperature after addition of 5 per cent. of benzoyl peroxide.

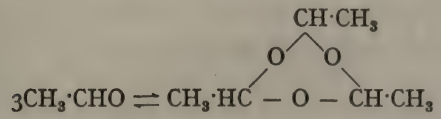
The rubbers obtained synthetically from isoprene and other similar hydrocarbons correspond not only to the supposed constitution of Para rubber, but also to various analogues of that substance, and exhibit differences in properties which depend upon the constitution of the hydrocarbon from which they are prepared by polymerization and the method by which this change is brought about. Harries[1] classifies synthetic rubbers in one or other of two groups: the first comprising the "normal" rubbers which are obtained by the polymerization of the unsaturated hydrocarbons brought about by heating them alone or along with acetic acid; the second including the "sodium" rubbers obtained by the action of the alkali metals, especially sodium, on the hydrocarbons. The two series are not identical, but exhibit various differences. Ostromisslenski,[2] in the course of a discussion of the different synthetic rubbers, claims that the product obtained by the polymerization of β-myrcene differs from all previous synthetic caoutchoucs, being perfectly identical with natural Para rubber. For further information on this point readers are referred to the interesting papers by these chemists, abstracts of which are contained in the *Journal of the Society of Chemical Industry* from 1911 onwards.

Polymerization of Aldehydes to Para-aldehydes.

Aldehydes of the aliphatic series are particularly prone to undergo polymerization, and the linking of the molecules can take place in different ways, so that there result compounds of the type of meta-aldehyde, para-aldehyde, and aldol, or of ethyl acetate. These reactions are brought about by the catalytic action of substances of very varied character, and frequently the presence of a mere trace of the catalyst is sufficient.

[1] *Ann.*, 1911, **383**, 157.
[2] *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1071.

The conversion of acetaldehyde into para-acetaldehyde, which is readily purified either by distillation or by crystallization, is of importance, firstly because para-acetaldehyde is frequently used instead of acetaldehyde itself in various synthetic reactions of technical value, and in the second place because the formation and subsequent decomposition of that compound affords a very convenient method for the purification of the aldehyde. The reaction is a reversible one, and the same catalyst which brings about the polymerization of the aldehyde in the cold induces the depolymerization of the para-aldehyde when it is heated



The acetaldehyde is cooled to a temperature of 4°–5°, and a few bubbles of dry hydrogen chloride are passed in, the introduction of the gas being stopped as soon as the temperature begins to rise quickly, which occurs after a few seconds. The aldehyde is left to stand in the cooling mixture for 4–5 hours, and then agitated with a little aqueous sodium carbonate, to remove all traces of acid, and then with a little water, dried over calcium chloride and distilled, or alternatively cooled until it solidifies, drained, and pressed in the cold. In either case all traces of hydrochloric acid must be removed. A simpler method of effecting the polymerization is to add to 1 litre of the aldehyde, water cooled, 5 c.c. of concentrated hydrochloric acid, and after half an hour 5 c.c. more. The liquid is left to stand over night and then washed and purified as before. Of course the aldehyde should be contained in a vessel with a reflux condenser attached. The temperature should not be lowered below 4°, otherwise formation of meta-aldehyde takes place. The yield is very good.

Pure aldehyde is readily obtained from the para-aldehyde by distillation after addition of a trace of sulphuric acid.

Polymerization of Acetaldehyde to Ethyl Acetate.

Acetaldehyde is converted almost quantitatively into ethyl acetate ($CH_3 \cdot CHO + OCH \cdot CH_3 = CH_3 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$) by means of small amounts of aluminium ethoxide in presence of catalysts, particularly the halogen compounds of aluminium, tin, or silicon, which are not by themselves capable of forming the ester from the aldehyde. For example, 6 parts of aluminium ethoxide, containing about 10 per cent. of aluminium, are added gradually to 135 parts of acetaldehyde; after standing for some hours the acetic ester is separated by distillation, the yield being about 123 parts. Instead of using the ethoxide and another catalyst the product obtained by treating it with water may be employed. The ethoxide is better employed in solution, preferably in ethyl acetate.[1]

A modified process [2] is the treatment of the aldehyde with a filtered solution of aluminium ethoxide in an organic solvent of high boiling point, *e. g.* nitrobenzene, xylene, or solvent naphtha, at temperatures between 0° and 15°, when it is claimed that a yield of 80 per cent. of the theoretical quantity of ethyl acetate may be obtained with a consumption of about 5 per cent. of the catalyst. Thus 400 parts of acetaldehyde are stirred gradually into a filtered solution of 16–20 parts of aluminium ethoxide in 45 parts of dry solvent naphtha, the mixture being kept below 15° by thorough cooling. After standing for about 24 hours the mixture is fractionally distilled; the first fraction contains acetaldehyde and may be used again, the next is almost pure ester, and the naphtha is recovered from the residue by steam distillation.

The catalytic activity of the aluminium ethoxide may be increased by dissolving in it, when in the molten state, anhydrous potassium alum, copper sulphate, camphor, etc., or by rapidly cooling the molten substance by pouring it on to a cold metal plate, or into a solvent, ethyl acetate being suitable for the purpose.[3]

[1] Eng. P. 26825 and 26826 (1913). [2] *Ibid.* 1288 (1915).
[3] *Ibid.* 4887 (1915).

Catalysis is also applied in the preparation of aluminium ethoxide, which is easily carried out by acting on anhydrous ethyl alcohol with aluminium in presence of a very small quantity of a catalyst, mercuric chloride, with or without the addition of ethyl halides or of iodine. The mixture is finally distilled under reduced pressure.[1]

Polymerization of Acetaldehyde to Aldol.

Now that aldol has been used as a source of butadiene and hence of a synthetic rubber, its formation is of practical importance. The union of two molecules of acetaldehyde with production of aldol—$2CH_3{\cdot}CHO = CH_3{\cdot}CHOH{\cdot}CH_2{\cdot}CHO$—is easily effected by treatment of the aldehyde with dilute solutions of potassium carbonate or bicarbonate, which act as catalysts.

Condensation

A number of the catalytic reactions already described as well as of those in the following chapter may be included in the extensive group of Condensations, and there are many other chemical changes of this type in which the " condensing agent " acts catalytically. A few additional examples may be given.

The synthesis of aromatic hydrocarbons by Friedel and Crafts' method, in which anhydrous aluminium chloride is employed as the catalyst, has already been mentioned, but it may be noted that this compound is still more widely used to catalyse the preparation of ketones by the interaction of an acid chloride and an aromatic hydrocarbon, *e. g.* $C_6H_6 + Cl{\cdot}CO{\cdot}CH_3 = C_6H_5{\cdot}CO{\cdot}CH_3 + HCl$. The reaction is usually carried out in presence of an indifferent solvent, such as carbon disulphide, light petroleum, or nitrobenzene, the last being particularly useful as it is a solvent for aluminnium chloride, and in many cases the aluminium choride may be replaced by anhydrous ferric chloride. Among the acid chlorides used in this way, carbonyl chloride is of considerable importance. Thus Crystal Violet can be prepared

[1] D. R. P. 286596.

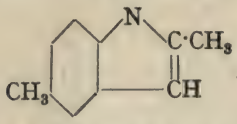
by warming a mixture of 40 parts of dimethylaniline, 10 parts of aluminium chloride and 6 parts of carbonyl chloride for 5–6 hours at a temperature of 20°–30°. The volatile products are then removed by steam distillation, and the dye salted out and recrystallized from water or converted into its sulphate or oxalate.[1]

$$COCl_2 + 3C_6H_5\cdot N(CH_3)_2 = \begin{matrix} N(CH_3)_2\cdot C_6H_4 \\ N(CH_3)_2\cdot C_6H_4 \end{matrix}\!\!>\!C{:}C_6H_4{:}N(CH_3)_2Cl + H_2O + HCl$$

Dilute hydrochloric acid acts as a catalyst in bringing about the condensation between alcohols and aromatic amines. For example, tetramethyltriaminotriphenylmethane can be prepared by warming on the water-bath a mixture of tetramethyldiaminobenzhydrol and aniline in presence of that acid. After the reaction is complete the liquid is made alkaline, the excess of aniline distilled off and the solid product collected and crystallized from benzene.[2]

$$\begin{matrix} N(CH_3)_2\cdot C_6H_4 \\ N(CH_3)_2\cdot C_6H_4 \end{matrix}\!\!>\!CH\cdot OH + C_6H_5\cdot NH_2 = \begin{matrix} N(CH_3)_2\cdot C_6H_4 \\ N(CH_3)_2\cdot C_6H_4 \end{matrix}\!\!>\!CH\cdot C_6H_4\cdot NH_2 + H_2O.$$

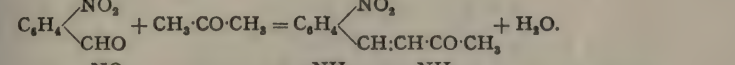
Hydrochloric acid also catalyses the condensation of aromatic ketones, or the corresponding secondary alcohols, with indole or its derivatives, which results in the production of dyes or the leuco-compounds of dyes. Thus 2·1 kilos of *p*-diaminobenzophenone and 1·5 kilos of 2:5-dimethyl-

indole,  , are dissolved in 20 kilos of hot alcohol, 5 gr. of concentrated hydrochloric acid added, and the solution heated nearly to boiling for three hours on the water-bath. Half of the alcohol is then distilled off, and the residual liquid stirred into water containing ice and

[1] D. R. P. 26016. [2] *Ibid.* 27032.

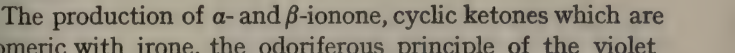
common salt. The dye which separates is filtered off, washed with a little solution of common salt, and dried at 40°–50°.[1]

Sodium hydroxide or other strong bases such as barium hydroxide act as catalytic agents in many condensation processes, sometimes even in very dilute solution and in very small quantities. Thus the first step in Baeyer and Drewsen's synthesis of indigotin consisted in condensing *o*-nitrobenzaldehyde with acetone by the addition of a small quantity of a dilute solution of caustic soda, the product readily undergoing further condensation with formation of the dye :—

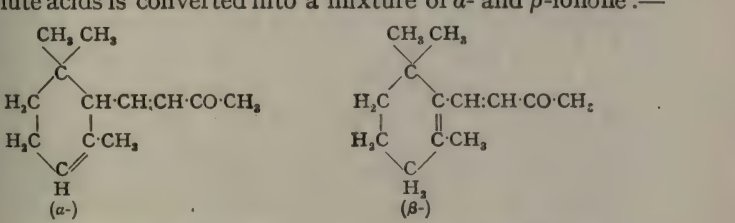


Halogen and other derivatives of *o*-nitrobenzaldehyde can be converted in a similar manner into corresponding derivatives of indigo.

The production of α- and β-ionone, cyclic ketones which are isomeric with irone, the odoriferous principle of the violet and which themselves have an odour of violets, has attained considerable technical importance. The first stage in the process is the condensation of citral, an unsaturated aldehyde contained in lemon-grass oil, with acetone, which takes place in presence of barium hydroxide [2] :—



The condensation product, pseudo-ionone, when heated with dilute acids is converted into a mixture of α- and β-ionone :—



[1] D. R. P. 127245, etc.

[2] *Ibid.* 73089.

Ammonia, and also primary and secondary amines, are effective in inducing the condensation of aldehydes with malonic or cyanacetic acids,[1] or their esters.[2] Thus cinnamic acid is obtained when 1 mol. of benzaldehyde and 1 mol. of malonic acid are mixed with 2 mols. of ammonia in about 8 per cent. alcoholic solution and heated in the water-bath until all has passed into solution. The alcohol is distilled off, and after about three hours the residue is heated until evolution of carbon dioxide has ceased. The product is dissolved in hot water and the acid liberated by addition of hydrochloric acid :—

$$C_6H_5{\cdot}CHO + CH_2(COOH)_2 = C_6H_5{\cdot}CH{:}CH{\cdot}COOH + H_2O + CO_2.$$

If the mixture is heated for an hour and a half at 55°–65°, the alcohol distilled off at the same temperature under reduced pressure, and the residue dissolved in water and precipitated by addition of acid, a yield of about 60 per cent. of the theoretical quantity of benzylidene malonic acid is obtained :—

$$C_6H_5{\cdot}CHO + CH_2(COOH)_2 = H_2O + C_6H_5{\cdot}CH{:}C(COOH)_2.$$

Similarly, the ethyl ester of citrylidene malonic acid is produced when citral is condensed with ethyl malonate in presence of a small quantity of ethylamine or of piperidine.

In order to obtain good yields of amyl acetate or acetates of higher alcohols by the interaction of chloropentane or its homologues with sodium acetate, the latter should be very porous and bulky. The salt is obtained in this form by adding anhydrous sodium carbonate to glacial acetic acid in approximately equivalent quantity, and, when the reaction is complete, heating the product for 8–12 hours without causing it to melt, the temperature being finally raised to about 140°. The efficiency of the porous salt thus obtained is greatly increased by catalytic agents, particularly copper salts. The catalyst may be added either before or during the preparation of the acetate, *e. g.* by adding copper carbonate to the sodium carbonate, or copper acetate to the

[1] D. R. P. 97735, 164296. [2] *Ibid.* 94132.

acetic acid; a suggested proportion is 3 parts of copper acetate to 72 parts of sodium acetate.[1]

In 1901 Grignard showed that magnesium reacts vigorously with alkyl and aryl halides in presence of ether at the ordinary temperature, and that the compounds produced, which have the general formula R.Mg.X. where R is an alkyl or aryl radicle and X a halogen radicle, are synthetic agents of the utmost importance. In the preparation of the "Grignard reagent" catalysts play an important part, some in promoting and others in hindering the reaction. Thus the reaction is retarded by the presence of substances such as anisole, ethyl acetate, chloroform and carbon disulphide; whilst, on the other hand, the presence of a trace of iodine often facilitates the interaction of magnesium and alkyl halides, and the addition of a trace of a magnesium alkyl halide promotes the formation of magnesium aryl halides, *e.g.* phenyl magnesium bromide. Moreover, as was shown by Baeyer, the interaction of halogen derivatives of aniline, dimethylaniline, etc., with magnesium can be brought about by "activating" the metal, that is to say, by depositing a thin film of magnesium iodide on its surface. It has also been discovered that the formation of magnesium organic compounds of this type can be brought about in inert solvents, such as benzene, light petroleum, etc., instead of in ether, through the catalytic action of tertiary amines, *e.g.* dimethylaniline. This mode of formation of the Grignard reagent has the advantage that subsequent operations can be carried out at higher temperatures than when ether is the solvent.

When passed over alumina heated to about 300° mixtures of acetylene with either sulphuretted hydrogen or sulphur vapour condense to form thiophen. The method is satisfactory for the production of thiophen on the large scale, since it yields a product containing only small proportions of higher homologues of thiophen and is not accompanied by perceptible charring of the acetylene. Under similar conditions mixtures of acetylene and steam yield furane,

[1] Eng. P. 2779 (1913), 3133 (1913).

and mixtures of acetylene and ammonia, when passed over alumina, ferric oxide, or chromic oxide, at temperatures slightly above 300°, give principally pyridine bases, consisting mainly of α- and γ-picolines together with 2-methyl-3-ethylpyridine.[1]

When a mixture of acetylene and sulphuretted hydrogen in the proportion of two volumes of the former to one volume of the latter is passed, at a temperature of 320°, over bauxite previously partially reduced by treatment with hydrogen at 380°, four-fifths of the liquid obtained by cooling the reaction gases distils below 95°, and is nearly pure thiophen, higher condensation products being formed only in small quantities.[2]

The production of the valuable synthetic resins known as Bakelite is based upon the condensation of phenol or cresol with formaldehyde or with such substances as trioxymethylene, methylal, and hexamethylene tetramine. The first products obtained are liquids or solids, and these under the influence of heat become hard insoluble and infusible substances of a high chemical and mechanical resistance. In order to bring about the condensation small quantities of alkalis, of substances with an alkaline reaction, or of substances which yield alkalis are employed. The products obtained differ somewhat in properties according to the nature of the condensing agent used.[3]

[1] Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 703.
[2] Eng. P. 109983 (1916).
[3] Cf. Lebach, *J. Soc. Chem. Ind.*, 1913, **32**, 559.

CHAPTER VII

Preparation of Hydrocarbons

One or two methods of preparing hydrocarbons, in addition to those referred to in previous pages, involve the use of catalysts.

The great demand for toluene has led not only to economies in its recovery from the products of the distillation of coal, but also to processes for obtaining it synthetically from the more abundant hydrocarbon benzene. One of the latter is based upon the well-known reaction of Friedel and Crafts, in which the action of alkyl halides on benzene is induced by the presence of anhydrous aluminium chloride, and indeed only differs from this process in so far that some iron turnings are added to the catalyst. Hydrochloric acid (only required in sufficient quantity to make up losses) is generated in a still and passed along with the acid liberated in the subsequent stages of the process through suitable drying towers, and then through vessels charged with fused zinc chloride and methyl alcohol; these vessels are heated by steam coils and connected with reflux condensers to condense any methyl alcohol which distils off. The methyl chloride formed is dried and passed through a series of towers provided with bubbling trays and charged with benzene and anhydrous aluminium chloride mixed with iron turnings; the towers are also heated by steam coils, so that the temperature of the benzene is maintained at 45°–55°. When the benzene in the first tower has been converted into toluene that tower is shut out of the series, and the toluene is drawn off, passed through a filter press, and washed to remove any dissolved hydrochloric acid; the tower is then recharged with benzene and connected last in the series. The hydrochloric acid from

the last tower is collected in a receiver and returned to the process at the beginning.[1]

According to another patent,[2] a chloro- or other halogen derivative of a hydrocarbon is heated to 150°–200° with a hydrocarbon in presence of phosphorus pentoxide, to act as a catalyst in the liberation of hydrochloric or other halogen acid. One gram-molecule of the halogen compound is said to require only from 2–3 gr. of commercial phosphorus pentoxide, whereas a much larger quantity of aluminium chloride would be necessary. The pentoxide is recovered by extracting the organic compound with a suitable solvent. Ketones are obtained in a similar manner by using an acid chloride in place of a chloro-derivative of a hydrocarbon.[2]

Preparation of Halogen Derivatives

The velocity of these reactions in which substitution derivatives of carbon compounds are obtained by the action of chlorine or bromine is greatly increased by the presence of small quantities of appropriate catalysts. Among the most commonly used "chlorine (bromine) carriers" are iron in the form of powder or wire, aluminium and amalgamated aluminium, tin, sulphur, iodine and iodine monochloride, the pentachlorides of phosphorus, antimony and molybdenum, aluminium chloride, ferric chloride, stannic chloride, and the corresponding bromides. These carriers all take part in the reaction, either through the formation of unstable compounds with the halogen, which in turn react with the carbon compounds, or by the continued formation and decomposition of the higher halide of the catalyst when more than one can exist, or by the formation of intermediate products, *e. g.* the compound of aluminium bromide and nitrobenzene, which readily enter into reaction with the halogen, the catalyst being liberated.

The following are examples of the employment of these catalysts.

In order to obtain monochloroacetic acid chlorine is passed into boiling acetic acid which contains a little sulphur in

[1] Eng. P. 8886, 9437 (1915). [2] D. R. P. 281802.

solution, or to which a little red phosphorus has been added. After about twelve hours the process is finished and the product is purified by distillation; 8 parts of acetic acid yield about 10 parts of monochloroacetic acid together with a little acetyl chloride. It is noteworthy that when chlorine is passed into cold acetic acid containing a little sulphur or sulphur chloride, acetyl chloride and not monochloroacetic acid is produced.

Chlorobenzene, which is used in large quantity, is prepared by the action of chlorine on benzene at the ordinary temperature and in presence of a catalyst. It is stated that the addition of a mixture of ferric chloride with finely divided iron facilitates the process to a remarkable extent. The reaction proceeds with regular evolution of hydrochloric acid and without any notable increase of temperature, so that external cooling is unnecessary. The process is interrupted before all the benzene in the reaction vessel has been chlorinated; the principal product is chlorobenzene, with only small quantities of dichloro-derivatives. After distillation at a temperature below 80° the catalyst remains as a dry mass in the vessel; as a result of the reaction it has gained in efficiency and can be used again with advantage.[1] As an example of the results of this process, 300 kilos of benzene containing 1 kilo of ferric chloride and 1 kilo of iron powder were treated with chlorine. The total yield, after two chlorinations of the first runnings from previous operations, was 335 kilos of chlorobenzene, 24 kilos of pure *p*-dichlorobenzene, and 13 kilos of a mixture of chloro-derivatives; 230 kilos of chlorine were used and 115 kilos of hydrochloric acid gas recovered.

A suitable catalyst for this process is prepared by mixing equal weights of iron, reduced by hydrogen, and of hydrated ferric chloride. These are thoroughly triturated in a mortar; at first liquefaction occurs, but after a time the temperature rises and the mass becomes solid. It is finely ground and carefully dried. A subchloride is said to be formed.[2]

m-Dinitrobenzene is rapidly converted into symmetrical

[1] D. R. P. 219242. [2] U.S. P. 1189251.

chlorodinitrobenzene if chlorine is led into the melted dinitro-compound in presence of iron wire, whereas in absence of the catalyst elimination of the nitro-groups occurs with formation of *m*-chloronitrobenzene and *m*-dichlorobenzene.[1] Dinitronaphthalene may be chlorinated in a similar way.[2]

Tetrachlorobenzaldehyde, a valuable intermediate for the manufacture of triphenylmethane dyes, is produced by the following series of reactions. Dry chlorine is passed over dry toluene containing anhydrous ferric chloride at 12°–15°, the mixture being stirred; when trichlorotoluene crystallizes out the mass is melted by heating to 45°–50°, then cooled to 35° and chlorine again passed in, the temperature being gradually raised to 50°, until the necessary increase in weight has been gained. On fractional distillation a yield of 90 per cent. of the theoretical quantity of tetrachlorotoluene is obtained. Further treatment with chlorine at 100°–130° in presence of light, particularly of ultraviolet rays, converts this compound into tetrachlorobenzylidene chloride; the corresponding aldehyde is produced by dissolving the chloride in concentrated sulphuric acid and pouring the solution into ice-cold water.[3]

In the preparation of benzyl chloride from toluene the presence of phosphorus trichloride facilitates the introduction of chlorine into the side chain and increases the velocity of the reaction. A rapid stream of chlorine is passed into a mixture of 100 parts of toluene and 1 part of phosphorus trichloride, heated to boiling and if possible exposed to sunlight, until the temperature of the liquid has risen to 155°. This requires from three to eight hours. After repeated distillation of the product about 80 parts of pure benzyl chloride, together with some benzylidine chloride and unaltered toluene are obtained.

In the chlorination of naphthalene in the state of vapour by means of chlorine, ferric oxide, cupric oxide, or pumice serve as catalysts.[4]

The employment of a catalyst is sometimes useful in

[1] D. R. P. 108165.
[2] *Ibid.* 134306.
[3] Eng. P. 16317 (1914).
[4] U.S. P. 914251.

additive reactions as well as in processes of substitution, for example, in the preparation of acetylene tetrachloride by the direct combination of acetylene with chlorine :—

$$CH{:}CH + 2Cl_2 = CHCl_2{\cdot}CHCl_2.$$

In the absence of catalysts this reaction may result in explosions, but in their presence proceeds more smoothly and has gained technical importance. When passed into acetylene tetrachloride containing some antimony pentachloride acetylene is absorbed, a double compound of acetylene dichloride and antimony pentachloride being formed; if chlorine is then passed into the mixture the double compound is broken down with formation of acetylene tetrachloride and liberation of the chloride of antimony. The alternate introduction of acetylene and of chlorine into the liquid is continued, and finally the acetylene tetrachloride is separated from the reaction product by fractional distillation. The chlorides of iodine, sulphur, or aluminium or iron may be used as catalysts instead of the chloride of antimony.[1]

Acetylene tetrachloride (sym. tetrachloroethane) is used as a solvent and also as the starting-point for the preparation of other compounds, di-, tri-, and tetra-chloroethylene and penta- and hexa-chloroethane, which are of practical importance. For example, when acetylene tetrachloride is heated to a high temperature, *e. g.* 300°, with the chloride of a tetravalent metal, the products are said to be pure trichloroethylene and hydrochloric acid only [2] :—

$$CHCl_2{\cdot}CHCl_2 = CHCl{:}CCl_2 + HCl.$$

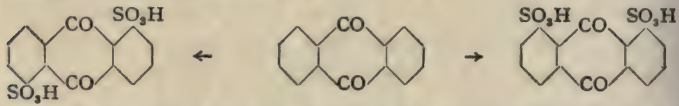
Sulphonation

In some cases, at least, catalysts are employed with advantage in the sulphonation of aromatic compounds; their influence is in the direction either of simply promoting the process, or in addition of affecting the course taken by the reaction.

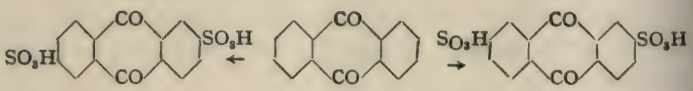
[1] D. R. P. 154657. [2] *Ibid.* 263457.

The sulphonation of benzene may be cited as an example of the former effect. It is claimed that the preparation of benzene monosulphonic acid may be carried out with weaker sulphuric acid and in a shorter time if a trace of iodine is added to the reaction mixture. Seventy parts of benzene, 146 parts of sulphuric acid, and 0·25 part of iodine are heated under a reflux condenser for five hours, when sulphonation is complete. The iodine is recovered by adding water to the product and filtering.[1]

The influence of a catalyst in modifying the course of the reaction is shown by the effect of the presence of mercury salts in the sulphonation of anthraquinone. If no catalyst is present acids containing the sulpho-groups in the β-positions to the carbonyl groups are obtained, but the addition of a little mercuric sulphate induces the formation of α-sulphonic acids; moreover, the reaction takes place at a lower temperature, and good yields are obtained with fuming sulphuric acid containing a smaller percentage of sulphuric anhydride. For example, when a mixture of 100 parts of anthraquinone, 200 parts of fuming sulphuric acid containing 40 per cent. of anhydride, and 1 part of mercury is heated slowly to 150°–160° and kept at that temperature for one hour, a mixture of the 1:5- and 1:8-anthraquinone disulphonic acids is obtained.[2]



On the other hand, if 100 parts of anthraquinone are heated with 200–300 parts of fuming sulphuric acid containing 45–50 per cent. of sulphuric anhydride at 160°–170° until a sample dissolves completely in water, without the addition of mercury, the product is a mixture of the 2:6- and 2:7-disulphonic acids:—



[1] Eng. P. 12260 (1915). [2] D. R. P. 149801, 157123.

In all probability the action of the mercury salt in this sulphonation process depends upon the formation of an intermediate mercury compound which then enters into reaction with the sulphuric acid.

In the sulphonation of benzoic acid also the position taken up by the sulpho-group is influenced by the presence of catalysts such as mercury salts. If the process is conducted without the addition of a catalyst practically nothing but the *m*- and *p*-sulphonic acids are produced, but if a little mercury is added as much as 7·5 per cent. of the *o*-acid is found in the product.[1]

The sulphonation of pyridine may be readily accomplished by heating it with sulphuric acid in presence of vanadyl sulphate. Poor yields are obtained if the pyridine is impure or if the heating is prolonged, when part of the sulphonic acid is completely destroyed and part reconverted into pyridine. Ferric sulphate also acts as a catalyst during the sulphonation, but at the same time decomposes the sulphonic acid, the latter effect becoming more pronounced when the period of heating is prolonged.[2]

Catalysts are sometimes effective in promoting the elimination as well as the introduction of sulpho-groups. Thus anthraquinone α-sulphonic acid is easily converted into anthraquinone when boiled with dilute sulphuric acid containing some mercuric sulphate, whilst in the absence of a catalyst the reaction is very incomplete; α-sulphonic acids of related compounds behave in a similar manner.[3]

Nitration

The following method of nitration is catalytic in character in so far as the oxides referred to may apparently be used for an indefinite period. Oxides of nitrogen diluted with air are absorbed by oxide of zinc, oxide of copper, or another metallic oxide of low basicity. The product is heated in an iron tube to 290°, a mixture of air and benzene vapour

[1] *Ber.*, 1907, **40**, 2413. [2] D. R. P. 160104.
[3] Meyer, *Monatsh.*, 1914, **35**, 765.

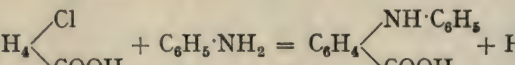
passed in, and the temperature raised slightly. Formation of nitrobenzene begins at 300°; the temperature must not be allowed to rise above 350°, otherwise decomposition sets in. The yield, calculated on the quantity of oxides of nitrogen used, is quantitative. If toluene is used instead of benzene, the product contains about 81 per cent. of *o*-nitrotoluene and 11 per cent. of *m*-nitrotoluene.[1]

Derivatives of Amines

The replacement of hydrogen in ammonia or amines by the phenyl group or by other aromatic radicles is not easily effected, but if a catalyst is added to the reacting mixture a very great increase in the velocity of the reaction is produced. Copper powder has been found of particular service in such cases; thus when *p*-nitroaniline is prepared by heating *p*-chloronitrobenzene with an excess of strong ammonia in an autoclave at a temperature of about 170° the reaction

is facilitated by the addition of metallic copper,[2] and again in the preparation of phenylglycine *o*-carboxylic acid by the interaction of *o*-chlorobenzoic acid and glycine the presence of a mere trace of the catalyst permits the reaction to be completed in one-fourth of the time required if copper is not added to the mixture.[3]

Phenylanthranilic acid is formed when copper powder is added to a boiling solution of *o*-chlorobenzoic acid in aniline:

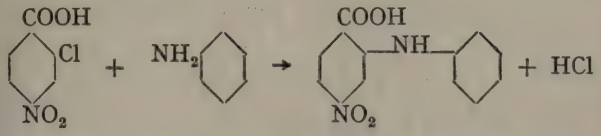


Salts of iron, nickel, platinum, and zinc also act as catalysts, whilst salts of manganese and tin do not; the best catalyst is copper, of which a trace suffices. The action is general

[1] D. R. P. 207170. [2] *Ibid.* 204591. [3] *Ibid.* 143902.

for the preparation of other aryl anthranilic acids, since other aromatic amines may be substituted for aniline. In order to obtain good yields, the addition of amyl alcohol or nitrobenzene to the mixture of amine and acid is of service.

Similarly, substitution derivatives of *o*-chlorobenzoic acid, *e. g.* 2-chloro-4-nitrobenzoic acid, or 2:4-dichlorobenzoic acid, yield with aniline, etc., substituted diphenylamine *o*-carboxylic acids[1]:—

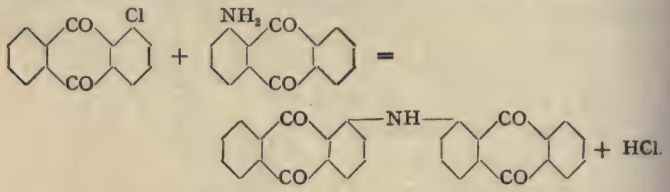


Not only metallic copper but also cuprous iodide and iodine have been recommended for use as catalysts in the preparation of various derivatives of amines, such as diphenylamine,[2] *p*-nitrodiphenylamine,[3] phenyl-*a*-naphthylamine,[4] and methyl or ethyl anilines.[5] Thus to prepare *p*-nitrodiphenylamine, 0·1 part of iodine is dissolved in 10 parts of *p*-chloronitrobenzene, 0·3 part of finely divided copper added, and the mixture heated until the coloration due to cuprous iodide appears. Then 75 parts of aniline and 5 parts of potassium carbonate are added, and the whole heated under a reflux condenser for 20 hours. The mixture is acidified with hydrochloric acid, the unchanged *p*-chloronitrobenzene driven off with a current of steam, and the residual *p*-nitro-compound crystallized from benzene or alcohol. Again, dimethylaniline is prepared by heating 93 parts of aniline, 96 parts of methyl alcohol, and 1 part of iodine for seven hours at a temperature of 230°. The product is separated from the water produced, and, after removal of the iodine with alkali, distilled under reduced pressure. The yield is said to be quantitative.

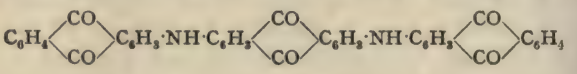
The method is applicable to the preparation of derivatives of naphthalene and of anthracene as well as of benzene, for it has been found that halogen and amino-derivatives

[1] Ullmann, *Ann.*, 1907, **355**, 312. [2] Fr. P. 374385.
[3] D. R. P. 185663. [4] *Ibid.* 241853. [5] *Ibid.* 250236.

of these hydrocarbons or of naphthaquinone or anthraquinone interact under the catalytic influence of small quantities of copper or copper salts; the reaction is generally carried out with addition of anhydrous sodium acetate and with or without a diluent such as nitrobenzene. Thus when 1-aminoanthraquinone is heated with 1-chloroanthraquinone a dianthraquinonylamine is obtained [1]:—



As a general rule compounds of this type possess no dyeing properties, but the condensation of two molecules of an aminoanthraquinone with one molecule of a dichloroanthraquinone or of two molecules of a chloroanthraquinone with one molecule of a diaminoanthraquinone gives rise to trianthraquinonylamines, several of which are important dyes, *e. g.* Indanthrene Red G., Indanthrene Bordeaux, etc.[2] For example, 20 kilos of 2-chloroanthraquinone, 10 kilos of 1:5-diaminoanthraquinone, 15 kilos of anhydrous sodium acetate, 3 kilos of cuprous chloride and 600 kilos of naphthalene or benzene are heated for 15–20 hours under a reflux condenser. The new compound obtained contains three anthraquinone residues linked by two NH groups [3]:—



Diazo-compounds

As a general rule the conversion of aromatic amines or their substitution derivatives into diazonium salts is readily effected, but in the case of aminonaphthol sulphonic acids a special difficulty arises, because nitrous acid has an

[1] Fr. P. 357138.
[2] Eng. P. 10324 (1906), 4235 (1907), 9219 (1909).
[3] Fr. P. 365919.

oxidizing action on these compounds and tends to produce naphthaquinone sulphonic acids; hence the yield of diazonium salt is frequently very poor.

This difficulty is overcome by carrying out the process of diazotization in the usual manner, but with the addition of a small quantity of a copper salt, usually copper sulphate. The catalyst not only accelerates the process, but also reduces the oxidizing action of the nitrous acid to a minimum or suppresses it completely. Iron or zinc salts may also be used as catalysts.[1]

The aminonaphthols themselves can be converted into diazo-oxides by diazotizing in presence of copper salts, whilst in absence of a catalyst the process only takes place with difficulty.[2]

The catalytic influence of cuprous salts (Sandmeyer) or of copper powder (Gattermann) in promoting the replacement of the diazo-group by the chlorine, bromine, or cyanogen radicle is of the greatest possible practical importance, but is so well known that mere mention of the use of catalysts in these reactions will suffice.

Catalysis of diazo-compounds is also employed in a process for the preparation of organic arseno-compounds, according to which a salt of arsenious acid or of an arylarsenious acid in solution or suspension is treated with a diazo-compound in presence of a catalytic agent such as copper powder, a copper compound, silver, etc.[3] The resulting compounds differ from those of the type $R{\cdot}As(OH)_2$ (*e. g.* $C_6H_4Br{\cdot}As(OH)_2$), prepared by the action of diazonium salts of substituted aromatic radicles on compounds containing the group $-As(OH)_2$ or $-As{:}O$,[4] in that they are readily reduced to arsenobenzene derivatives by hydrosulphites in the cold.

Preparation of Aldehydes and Ketones

In a previous chapter it has been shown that aldehydes and ketones may be obtained by catalytic dehydrogenation

[1] D. R. P. 171024, 172446, 175593.
[2] *Ibid.* 172446.
[3] *Ibid.* 254092.
[4] Eng. P. 568 (1911).

of primary and secondary alcohols respectively at high temperatures, but this is not the only method of preparing those compounds in which the presence of catalysts is of service.

Benzaldehyde is usually prepared from toluene by conversion of the hydrocarbon into benzylidene chloride and subsequent hydrolysis of the latter with water containing milk of lime: $C_6H_5{\cdot}CHCl_2 + H_2O = C_6H_5{\cdot}CHO + 2HCl$. It has been found that the hydrolysis of the chloride is greatly accelerated by the addition of a small quantity of finely divided iron, and that in this case it is not necessary to add milk of lime to the water. The process is carried out as follows: 60 kilos of crude benzylidene chloride are heated by indirect steam to 20°–25°, 20 gr. of powdered iron are added, and the whole covered with 10–15 kilos of water. The vessel containing the mixture is connected with an apparatus for the absorption of hydrochloric acid, and the temperature raised to 90°–95°. The reaction proceeds rapidly, and when the evolution of hydrochloric acid has ceased the contents of the vessel are made alkaline by addition of milk of lime (prepared from 9–10 kilos of quicklime) and the benzaldehyde distilled over with steam. Crude benzylidene chloride always contains benzotrichloride, which is also hydrolysed with formation of benzoic acid,

$$C_6H_5{\cdot}CCl_3 + 2H_2O = C_6H_5{\cdot}COOH + 3HCl,$$

which, of course, reacts with the calcium hydroxide to form calcium benzoate. After removal of the benzaldehyde, the residue is filtered and the filtrate acidified with hydrochloric acid, when benzoic acid separates.

The same process is used to prepare benzoic acid from commercial benzotrichloride, with the modification that a considerable quantity of milk of lime is introduced from the start, in order to neutralize the acids produced by the hydrolysis of the trichloride; this accelerates the reaction and protects the walls of the vessel from corrosion. For example, 20 gr. of powdered iron are added to a mixture of 60 kilos of benzotrichloride and 200 kilos of milk of lime, containing

34 kilos of lime. At the start heat is applied by means of a steam jacket, but this is soon discontinued because the heat of the reaction is sufficient to allow the process to continue once the temperature of the mixture has been raised to 50°. When the reaction is complete the benzaldehyde formed by hydrolysis of the benzylidene chloride present in commercial benzotrichloride is removed by a current of steam, the mixture filtered, and the benzoic acid precipitated by addition of hydrochloric acid.[1]

In order to dispense with the more expensive toluene, several methods have been devised for the direct production of benzaldehyde from benzene; two of these, which involve the use of aluminium chloride as catalyst, are due to Gattermann.

By passing a mixture of carbon monoxide and hydrochloric acid into aromatic hydrocarbons of the benzene series in presence of cuprous chloride and aluminium chloride aldehydes of the benzene series are formed. The mixture of HCl and CO acts on the hydrocarbon as if it were the hypothetical formyl chloride, H·CO·Cl; thus:—

$$C_6H_6 + H{\cdot}CO{\cdot}Cl = C_6H_5{\cdot}CHO + HCl.$$

For example, a mixture of dry hydrogen chloride and carbon monoxide is passed through a mixture of 10 kilos of benzene, 10 kilos of aluminium chloride and 1 kilo of cuprous chloride at a temperature of 40°–50° for about six hours, the whole being well stirred; a further quantity of 5 kilos of aluminium chloride and 0·5 kilo of cuprous chloride is then added and the mixed gases passed through for other six hours. The mass is then poured into ice water and steam distilled; the benzaldehyde is separated from the unchanged benzene which passes over by means of sodium hydrogen sulphite.[2]

Aromatic aldehydes are also obtained by acting on aromatic hydrocarbons, phenol ethers, etc., with a mixture of hydrocyanic acid and hydrochloric acid in presence of aluminium chloride and decomposing the compounds

[1] D. R. P. 82927, 85493. [2] Eng. P. 13709 (1897).

produced by means of acids. The mixed acids, in the gaseous state, are allowed to act on the mixture of the hydrocarbon and aluminium chloride for several hours at a temperature of 35°–40°. The mixture of HCl and HCN behaves as if it were imino-formyl chloride, NH:CHCl, yielding with the hydrocarbon an imino-derivative of the aldehyde :—

$$C_6H_6 + NH{:}CHCl = C_6H_5{\cdot}CH{:}NH + HCl;$$

this imino-derivative is then hydrolysed by the action of aqueous acids : $C_6H_5{\cdot}CH{:}NH + H_2O = C_6H_5{\cdot}CHO + NH_3$.

The process is specially suitable for introducing the CHO group into phenol ethers.[1]

It is also claimed that aromatic aldehydes are obtained by the action of carbon monoxide under increased pressures, *e. g.* from 40 to 90 atmospheres, on aromatic hydrocarbons or their substitution derivatives in presence of aluminium chloride : $C_6H_6 + CO = C_6H_5{\cdot}CHO$. The presence of a little hydrochloric acid is sometimes an advantage. Good results are said to be obtained in cases where Gattermann's process fails or gives unsatisfactory yields.[2]

A well-known method for the production of ketones is the distillation of the calcium or barium salts of organic acids : $\begin{matrix} R{\cdot}COO \\ R{\cdot}COO \end{matrix}\!\!>\!Ca = R{\cdot}CO{\cdot}R + CaCO_3$. At high temperatures monobasic acids themselves break down, partly into ketones, carbon dioxide and water, and partly into hydrocarbons and carbon dioxide, but under these conditions the ketones and the hydrocarbons are also more or less completely decomposed and complex mixtures of products result. In presence of suitable catalysts, however, the decomposition of acids is facilitated, and the process may be applied with advantage in the preparation of many simple and mixed ketones.

Such a catalytic decomposition of acetic acid was described by Squibb more than twenty years ago.[3] According to this

[1] Eng. P. 19204 (1897). [2] *Ibid.* 3152 (1915).
[3] *J. Soc. Chem. Ind.*, 1895, **14**, 506; 1896, **15**, 612.

observer the vapour of acetic acid passed through a tube heated to about 500° suffers only a small amount of decomposition. The decomposition is increased when the tube is filled with pumice, and becomes nearly complete when barium carbonate is present in addition, the acid breaking down into acetone, carbon dioxide and water :—

$$2CH_3{\cdot}COOH = (CH_3)_2CO + CO_2 + H_2O.$$

The yield of acetone is about 90 per cent. of the theoretical quantity. Apparently the carbonate of any other metal of which the acetate yields acetone on distillation, or such acetates, may be used as catalysts instead of barium carbonate. The temperature of decomposition appears to vary with the character of the carbonate employed and also with its physical state.

These observations have been extended by Senderens and by Sabatier and Mailhe,[1] who showed that whilst the alkaline earth carbonates are very good catalysts for acetic acid, precipitated chalk, for instance, at 450° transforming the acid into practically pure acetone, with propionic acid the yield of the corresponding ketone is less satisfactory, and with the higher fatty acids still less so. On the other hand, zirconia and particularly thoria act as efficient catalysts in the production both of fatty ketones, of mixed fatty-aromatic ketones, and to some extent of aromatic ketones, and may be used at temperatures below 400°, even at 200°. Moreover, other oxides may be used with very good results; thus ferric oxide in many cases gives satisfactory yields, and when it fails manganous oxide may be employed. The latter oxide, indeed, appears to be an excellent catalyst for the production of ketones from both fatty and aromatic acids, or mixtures of these. The vapours of the acid are passed over a layer of manganous oxide about 60 cm. long heated to 400°–450°. The oxide may be used repeatedly, and since little carbonization or polymerization occurs the yields of the ketones are in most cases almost quantitative.

[1] *Compt. rend.*, 1912, **154**, 1518; 1914, **158**, 830.

Mailhe has also discovered that the employment of titanium dioxide as a catalyst leads to a general method for the production of aldehydes from acids. The vapour of the acid to be transformed, mixed with an excess of the vapour of formic acid, is passed over a layer of titanic oxide heated to a temperature of 300°. Carbon monoxide and carbon dioxide escape, and the condensed product contains water, the aldehyde, and unchanged acids, from which the aldehyde can be easily separated :—

$$R{\cdot}COOH + H{\cdot}COOH = R{\cdot}CHO + CO_2 + H_2O.$$

Aldehydes containing up to nine carbon atoms have been prepared with yields varying from 40 to 90 per cent., but apparently the aromatic acids do not give good results.

Sulphur Compounds

Another group of reactions in which the influence of catalysts has proved to be of value includes the preparation of various classes of organic sulphur compounds. Among these the " vulcanization " of rubber occupies a prominent place; the following will serve as examples of other processes.

Thiosalicylic acid, $C_6H_4\begin{<}SH\\COOH\end{>}$, may be prepared from *o*-chlorobenzoic acid by the action of alkali hydrosulphides in presence of copper or copper salts. For example, 50 kilos of chlorobenzoic acid are converted into the sodium salt by the addition of the necessary quantity of a solution of sodium hydroxide (40° Bé.); 100 kilos of potassium hydrogen sulphide, and 0·2–0·5 kilo of copper sulphate in solution, or an equivalent quantity of finely divided copper are added and the mixture is heated very gently to a temperature of 150°–200° and finally to 250°, when the mass gradually solidifies. The product is dissolved in 1000 l. of water, and the solution filtered and acidified, when a quantitative yield of the thio-acid is obtained.[1]

[1] D. R. P. 189200.

Sulphurized dyes, which dye cotton from a sulphide bath in red shades, are obtained when hydroxylated azines, or their alkyl, aryl, carboxylic or sulphonated derivatives, or oxy-derivatives of substances containing an azine group, are heated with alkali polysulphides in presence of nickel or cobalt or a compound of either, or of mixtures of these metals or their compounds. For example, 50 parts of sulphur are dissolved in 100 parts of crystallized sodium sulphide and 66 parts of water : then 20 parts of aminohydroxyphenazine are introduced, and finally 8 parts of crystallized cobalt sulphate dissolved in 16 parts of water. The mass is heated to 120° for about fifteen hours.[1]

The Vulcanization of Rubber.[2]

The influence of catalysts in accelerating the process of vulcanizing rubber has received considerable attention, especially in recent years, because in practice it is desirable that the period necessary for satisfactory vulcanization should not be too prolonged.

The resins and protein substances which occur in natural rubber appreciably affect the rate of vulcanization. If these, and especially the proteins, are removed there is a marked decrease in the velocity of the process, whereas if the proportion of protein in a natural rubber is increased by removal of part of the hydrocarbon the rate of vulcanization is increased. Apart, however, from these natural catalysts, others both inorganic and organic have been for long in use.

The successful development of the rubber industry dates from the year 1839, when Goodyear discovered the process of vulcanization. The main drawback to the original method (mixing the rubber with suitable proportions of sulphur, and subjecting the mixture to a temperature from 135° to 140° for periods of time varying with the quantity of sulphur used) is the rather long period of heating required

[1] Eng. P. 17749 (1907).

[2] Twiss, *J. Soc. Chem. Ind.*, 1917, **36**, 783; Peachey, *J. Soc. Chem. Ind.*, 1917, **36**, 425, 950.

for complete vulcanization. Goodyear himself recognized that the process could be hastened by the addition of magnesia to the mixture of rubber and sulphur, and for many years past manufacturers have employed this catalyst, as well as litharge, lime, and to a smaller extent magnesium carbonate, as "accelerators" or sulphur carriers. Apart from these basic compounds the only inorganic accelerators which have been proposed are various metallic iodides, in particular antimony iodide, but these do not appear to have come into general use. These accelerators when added to mixtures of rubber and sulphur in quantities of from 5 per cent. upwards reduce very considerably the time required for vulcanization, but their use is necessarily restricted to the manufacture of certain classes of rubber goods owing to the fact that they produce other and undesirable effects.

In recent years a notable advance in the process of heat vulcanization of rubber has been the introduction of organic bases as accelerators. The first patent[1] bearing on this practice claimed the use of piperidine; subsequently the employment of many different amines was protected, and a later patent[2] covers the application of all organic bases of dissociation constant exceeding 1×10^{-8}, for example, *p*-phenylene diamine, aldehyde-ammonia, benzylamine, and naphthylene diamine. Volatile or unstable bases may be used in the form of such derivatives as carbamides, dithiocarbamides, carbamates or carbonates; thus the unstable base aminoguanidine is an excellent catalyst when used in the form of its comparatively stable bicarbonate. One of the most powerful of these organic catalysts is aldehyde-ammonia, of which the effectiveness far surpasses what might be anticipated from its ammonia content.

The activity of most of the known organic catalysts is in some way related to the possession of basic or alkaline properties, and the dissociation constant referred to above forms a dividing line between bases which act as accelerators and those which do not. Undoubtedly, however, there

[1] Eng. P. 11530 (1913). [2] *Ibid.* 11615 (1913).

exists another class of organic accelerators, represented at present by certain compounds which contain the nitroso-group directly linked to a benzene nucleus or a similarly constituted nucleus. (The nitroso-amines, in which the nitroso-group is linked to a nitrogen atom, are inert.) Of these compounds *p*-nitrosodimethylaniline is probably the most effective.[1] Thus, according to Peachey, whilst a mixture of 100 parts of rubber and 10 parts of sulphur normally requires to be kept at 140° (40 lbs. steam pressure) for one hour when a "soft cure" is desired, or longer in the case of a harder cure, if from 0·3 to 0·5 per cent. of *p*-nitrosodimethylaniline is incorporated before heating the mixing it can be completely vulcanized in about twenty minutes. Similarly a vulcanite mixing (100 parts of rubber and 40 parts of sulphur) which normally requires to be heated at 140° for six hours may be completely cured in about two hours by the previous addition of 0·75 per cent. of the nitroso-compound. Generally speaking, the addition of 0·5 per cent. or less of the catalyst to any mixing of good quality suffices to reduce the time necessary for vulcanization to one-fourth or one-third of that normally required.

A modified form of the catalyst is prepared [2] by heating a mixture of *p*-nitrosodimethylaniline with a certain proportion of sulphur to a temperature of about 130°, when vigorous reaction occurs with evolution of a reddish vapour which condenses on cooling to a yellowish-red solid. The residual reddish-brown mass by extraction with acetone or chloroform and subsequent evaporation of the extract yields a dark brown viscous mass. Both the yellowish-red condensate and the viscous mass act as powerful accelerators of the vulcanizing process, when a small quantity of either is added to a rubber mixing previous to heating.

The organic accelerators differ from such substances as magnesia or oxide of lead in so far that exceedingly small quantities are effective; their action is apparently truly catalytic in character. In this connection it should be noted that certain organic compounds possess the property

[1] Eng. P. 4263 (1914). [2] *Ibid.* 113570 (1917).

of retarding vulcanization, that is to say, appear to act as anticatalysts; among such are phenylhydrazine, methylene blue, and glucose.

As already indicated, most of the effective organic catalysts are basic in character, and their activity is roughly proportional to their alkalinity, a relatively feeble base like aniline having little influence on the rate of vulcanization; the inorganic accelerators in common use are also basic in character. Bearing these facts in mind, Twiss was led to attribute the relative advantage attaching to the use of organic bases chiefly to the fact that these substances are soluble in rubber, whereas the inorganic catalysts being sparingly soluble are not so uniformly distributed through the mass. He therefore concluded that the alkali hydroxides would prove to be excellent accelerators if a solvent for these compounds could be found which would itself dissolve in rubber, and finally patented [1] the use of glycerol, which dissolves approximately 25 per cent. of potassium hydroxide and a smaller proportion of sodium hydroxide. If from 1 to 2 per cent. of this solution is added to a rubber-sulphur mixture the vulcanization process is strongly accelerated, the effect being comparable with that of the strongest organic accelerator.

Intramolecular Rearrangements

Intramolecular rearrangements, resulting in the transformation of carbon compounds into their isomerides, are also included among the reactions in which catalysts take part, and some reactions of this type are of technical importance. Familiar instances are the conversion of hydrazo-compounds into benzidine or its derivatives through the catalytic influence of strong acids,

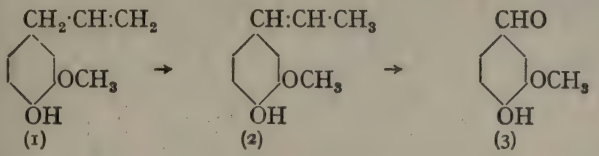
$$C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5 \rightarrow NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2,$$

and the formation of aminoazo-compounds where diazoamino-compounds are warmed with a mixture of an amine and its hydrochloride :—

$$C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5 \rightarrow C_6H_5{\cdot}N{:}N{\cdot}C_6H_4(NH_2).$$

[1] Eng. P. 17756 (1916).

Again, one of the methods of preparing vanillin (3), which is so largely used as a flavouring material, is the oxidation of isoeugenol (2), which is obtained by heating the isomeric eugenol (1) with potassium hydroxide in amyl alcoholic solution :—



A more recent example is the production of isoprene from the isomeric unsymmetrical dimethylallene, which is effected by passing the latter over heated catalysts, preferably under reduced pressure, and under such conditions as to avoid the formation of polymerized hydrocarbons; alumina and aluminous compounds are specially suitable as catalysts : [1] $(CH_3)_2C{:}C{:}CH_2 \rightarrow CH_2{:}C(CH_3){\cdot}CH{:}CH_2$.

Enzymes [2]

Some very important chemical operations are carried out through the agency of one or other of the group of catalysts known as enzymes; among such operations are included the preparation of ethyl alcohol (together with higher alcohols) from starch, of maltose from starch, of acetic acid from ethyl alcohol, of lactic acid or butyric acid from lactose, of citric acid from dextrose, and of indigotin from the glucoside indican which occurs in the sap of the indigo plant.

Enzymes are catalysts produced by living organisms, and in all probability are substances of definite chemical composition; in many respects their action resembles that of inorganic catalysts, and especially of such metals as platinum when in the colloidal state. As enzymes are themselves colloids, the reactions catalysed by them belong to the class of heterogeneous catalysis. They are specific in their

[1] Fr. P. 440130.

[2] Cf. Bayliss, *The Nature of Enzyme Action.*

action; that is to say, a certain definite enzyme is required to bring about a particular transformation.

As in the case of inorganic catalysts, a very small quantity of an enzyme will transform a relatively large amount of the substance undergoing change, and in general the velocity of the reaction is proportional to the quantity of the catalyst present, whilst the final result is independent of that quantity. Enzymes also, like many inorganic catalysts, are very sensitive to the action of " poisons," such as hydrocyanic acid, sulphuretted hydrogen, mercuric chloride, etc.; moreover, in many cases their activity is enhanced by the presence of small quantities of promoters. For instance, the efficiency of lipase in hydrolysing fats is increased by the addition of a trace of manganous sulphate, and trypsin, which is practically inert in acid or neutral solutions, is greatly assisted in its action by the presence of alkalis. Autocatalysis, positive or negative, plays a considerable part in the changes of activity of an enzyme during the course of its action.

There are, however, certain differences between enzymes and inorganic catalysts, some of which undoubtedly arise from the character of the former as organic colloids. Enzymes are sensitive to heat. In catalysis with these substances rise of temperature up to a certain point increases the rate of change, and for each enzyme there is a particular optimum temperature, frequently in the neighbourhood of 40°, at which its activity is at a maximum. At higher temperatures, from 60° to 100°, they are as a rule gradually destroyed, but some under certain conditions are able to withstand the temperature of boiling water. Moreover, although enzymes resemble ordinary catalytic agents in being active in very small concentrations, they lose their activity when a certain amount of the substance on which they act has been transformed; this amount may be large, but is not, as in the case of inorganic catalysts, practically without limit. In many cases the enzyme itself disappears in the course of the reaction.

As regards the mechanism of enzyme action much remains to be discovered, but there is considerable evidence that a combination of some kind is formed between the enzyme

and the substance on which it exerts its activity preparatory to the action of the former. There is also similar combination between the enzyme and the products of the transformation.

Surface Combustion

Catalysis appears to play a part in the production of light by means of incandescent mantles, and undoubtedly does so in processes of surface combustion.

An ordinary incandescent mantle contains about 1 per cent. of ceria, and smaller quantities of glucina and alumina, the remainder being composed of thoria; in mantles designed for use with high-pressure gas the proportion of ceria is increased, and may reach nearly 3 per cent. Pure thoria does not glow brightly when heated. It acquires the property of becoming highly luminous at high temperatures only when mixed with small quantities of other metallic oxides, of which ceria is by far the most efficient. It is supposed that the ceria exercises a catalytic influence of some kind or another, but at present nothing more than a guess at the nature of that influence is justified.

The catalytic influence of surfaces on chemical reactions finds important application in the now well-known methods of surface combustion, of which the development is chiefly due to Bone.[1] As the result of a series of investigations on the influence of various heated surfaces on the combustion of hydrogen and of carbon monoxide, that observer came to the following general conclusions.

(1) All surfaces have the power of accelerating gaseous combustion, in varying degrees depending upon their chemical character and their physical structure.

(2) The combustion takes place only in layers immediately in contact with the incandescent surface and not equally through the system.

(3) The acceleration of surface combustion depends upon

[1] Cf. Howard Lectures, Royal Society of Arts, March 1914.

an absorption of the combustible gas and probably also of oxygen by the surface, whereby the gases are activated.

(4) The surface becomes electrically charged during the process.

It has also been found that the power possessed by hot surfaces of accelerating gaseous combustion is exhibited in an increasing degree as the temperature rises, and that the marked differences between the catalytic power of various surfaces at low temperatures gradually diminish with rise of temperature and practically disappear when bright incandescence is reached.

Incandescent surface combustion has been applied to a number of practical purposes such as the concentration of solutions, raising steam, melting metals, etc.

In one method a porous diaphragm of refractory material, fitted into a suitable frame which provides a space at the back into which the mixture of gas and air can be fed, is brought into proximity to the object to be heated. The gas is first turned on and lighted and then air gradually added until the quantity necessary for complete combustion, or a slight excess, is present. The flame becomes non-luminous and diminishes in size, and almost immediately retreats to the surface of the diaphragm, and finally all signs of flame disappear, whilst the surface glows intensely. The temperature thus attained is very high, and practically no solids have been found suitable for the contact material except calcined magnesia and carborundum.

In a second form of the apparatus, more particularly adapted for raising steam or melting metals, the porous diaphragm is replaced by granules of the refractory contact material, which may be arranged in layers or packed into tubes, *e.g.* in a tubular boiler. In an arrangement which provides for the use of liquid fuel, the fuel is burnt in a separate space under the boiler, and the products of combustion are carried with the requisite proportion of air through boiler tubes charged with the granular contact surface.

This method of surface combustion admits of the employment of almost any form of combustible gas, such as waste

gases from blast furnaces and coke ovens and producer gas of all kinds, and a high efficiency is obtained.

Whatever the explanation of the mechanism of the process may be—possibly the formation of layers of electrically charged gas may induce greatly increased chemical activity—there is no doubt that the influence of the heated surface is catalytic in character.

LIST OF THE PRINCIPAL CATALYSTS OF WHICH APPLICATIONS ARE ILLUSTRATED

Acetic acid
„ anhydride
Acids, inorganic
„ , organic
Alcohol
Aldehyde-ammonia
Alkalis
Alkali metals
„ „ , salts of
Alkaline earth metals
„ „ „ , salts of
Alumina
Aluminium
„ bromide
„ chloride
„ ethoxide
„ silicate
„ sulphate
Amines
Aminophenols
Ammonia
Ammonium molybdate
Anhydrides of organic acids
Animal charcoal
Antimony iodide
„ pentachloride

Barium chloride
„ hydroxide
„ peroxide
„ oxide
Bases
Bauxite
Benzaldehyde
Benzoyl peroxide
Benzylamine
Bog iron ore
Boric acid
„ oxide
Broken brick
Bromine
Burnt pyrites

Cadmium
Calcium carbonate
„ chloride
„ fluoride
„ hydroxide
„ oxide
Camphor
Carborundum
Ceria
Ceric sulphate
Cerium
Charcoal
Chloroplatinic acid
Chromic acid
Chromium
„ sesquioxide
Clay
Cobalt
„ oxide
„ salts
„ soap
„ suboxide
„ sulphate
Coke
Copper
Cupric acetate
„ oxide
„ sulphate
Cuprous chloride
„ iodide
„ oxide

Diamines
Dimethylaniline
Dyes

Earth metals
„ „ , oxides of
Enzymes
Ethylamine

Ferric chloride
„ oxide
„ sulphate
Ferroso-ferric oxide

Ferrous chloride
,, oxide
,, salts
Formic acid

Gelatin
Glucina
Glucinum chloride
Gold

Hydriodic acid
Hydrochloric acid
Hydrofluoric acid

Iodine
,, monochloride
Iron
Iron-bismuth
Iron-cerium
Iron-copper couple
Iron disulphide
,, , magnetic oxide of
,, ore, hydrated
,, oxide
Iron + promoters
Iron-thorium

Kaolin

Lead
,, oleate
,, oxide
Lime
,, + charcoal
,, + metallic oxide
Litharge
Lithium chloride
Lithium-manganese nitride
Lixiviated alkali ferrite

Magnesia
Magnesium
,, alkyl halides
,, carbonate
,, iodide
Manganese
,, dioxide
Manganous acetate
,, linoleate
,, oxide
Mannitol
Mercuric acetate
,, chloride
,, nitrate
,, sulphate
Mercury
Mercury salts of sulphonic acids
Molybdenum
,, nitride
,, oxide
,, pentachloride
Molybdic acid

Naphthylene diamines
Nickel
,, + promoters
,, acetate
,, chloride
,, formate
,, lactate
,, oxide
,, soaps
,, suboxide
Niobium (columbium)
Nitrogen, oxides of
Nitrosodimethylaniline
Nitrosyl chloride
Nitrous acid

Organic bases
,, sulphur compounds
Organo-metallic compounds
Osmates, alkali
Osmium
,, tetroxide

Palladious chloride
,, hydroxide
Palladium
Palladium-nickel
Palladium-platinum
Phenylene diamine
Phosphoric acid
Phosphorus, red
,, pentachloride
,, pentoxide
,, trichloride
Platinic chloride
Platinous chloride
,, hydroxide
Platinum
Platinum-iridium
Potassium
,, carbonate
,, chloroplatinate
,, chromate
,, cyanide
,, fluoride
,, hydroxide
,, sulphite
Pumice
Pyrites cinder

Red lead
Rhodium
Ruthenates, alkali
Ruthenium

Sand
Silica
Silicates
Silver
Silver-iron couple
Sodium
„ carbonate
„ chloride
„ hydroxide
„ molybdate
„ phosphate
„ resinate
„ vanadate
Sodium-zinc ethyl
Spathic iron ore
Stannic chloride
„ oxide
Stannous chloride
Sulphanilic acid
Sulphonic acids
Sulphur
„ chloride
Sulphuric acid

Tantalum
Thallium chloride
Thoria
Tin
Titanates
Titanium dioxide
Titanous sulphate
Trioxymethylene
Tungsten
„ nitride
„ oxide
„ pentoxide

Uranium
„ carbide
„ nitride
„ oxide

Vanadates
Vanadic acid
Vanadium pentoxide
„ salts
„ trioxide
Vanadyl sulphate

Water
Weldon Mud

Zinc
„ oxide
„ salts
Zircon
Zirconia

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